

and the scientific literature, for the production of pseudo-ionones, sodium ethylate is the most satisfactory. It is found that metallic sodium is very efficient. The method and technique of this condensation have been improved and good yields of much purer products obtained. The bisulfite method of purification is capable of general application in the purification of pseudo-ionones.

3. One of the best catalytic agents for the conversion of pseudo-ionones into ionones is 85% phosphoric acid; the conditions necessary for high yields and purity are indicated.

4. The actions of alkaline condensing agents on mixtures of citral and dimethyl ketone, methylpropyl ketone, acetophenone, diethyl ketone and dipropyl ketone, have been investigated. From the second and third, new ionones have been synthesized, the one from methylpropyl ketone having an agreeable violet odor, while that from acetophenone merely suggests the presence of such a fragrance.

5. It is thus evident that the introduction of propyl in place of methyl in ordinary ionone does not materially affect the character of the odor, while that of phenyl causes it to disappear almost completely.

6. Furthermore, those ketones, in which both alkyl groups attached to the —CO— group are other than methyl, condense with citral only with great difficulty, or not at all, this behavior being in harmony with their incomplete condensation with benzaldehyde and other reagents. Thus diethyl ketone apparently reacts, but with considerable difficulty while dipropyl ketone cannot be induced to undergo condensation.

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THE CAUSATION OF ORGANIC REACTIONS BY ALUMINA, AND THEORIES OF CATALYSIS

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After a considerable experience in the use of the difficultly reducible oxides, alumina, titania, and thoria, as catalysts the conclusion was reached that the differences attributed to the oxides by Sabatier were due to modifiable physical characteristics rather than to distinctive chemical differences.¹ In experimental verification of this idea we were able to activate alumina selectively for the two reactions in the decomposition of ethyl acetate at the surface of alumina by modifying as we believe the spacial relationships of the molecules or "active points" of the catalyst.² Six dis-

¹ Adkins, *THIS JOURNAL*, **44**, 385 (1922).

² Adkins, *ibid.*, **44**, 2175 (1922).

tinct types of catalytic alumina have been prepared from hydrated alumina, aluminum hydroxide and various aluminum alkoxides. These types were prepared in working upon the hypothesis that in making alumina from aluminum hydroxide or alkoxides the distance between the aluminum atoms (or alumina molecules) in the catalyst would be determined in part by the size and shape of the radical attached to the aluminum when the compound went into the solid state. These types gave ethylene from 0.35, 0.42, 0.50, 0.64, 1.06 and 1.45 as many molecules of the ethyl acetate as they gave carbon dioxide and acetone. Yet this change in relative activity was not accompanied by any corresponding change in the amount of ester reacting. For example (see Table I) Catalyst 1 caused 21.2 g. of ethyl acetate to react in one hour, while Catalyst 2 caused 20.5 g. to react. In the former case the ratio representing the proportion of molecules giving ethylene to those giving carbon dioxide is as 1:0.35, while in the latter it is 1:1.45. This means that both of the catalysts adsorbed approximately the same amount of the ester but that the two catalysts presented different spacial arrangements upon their surfaces and hence induced to different degrees the possible reactions. It should be noted that the degree of activity as measured by the amount of ester reacting in unit time is not usually precisely reproducible but that the ratio of the products can be duplicated with great accuracy. In some twenty or more preparations of Catalyst 1 the activity has varied in different preparations by as much as 100% while the ratio has varied from 0.34 to 0.37.

The idea that the spacing of atoms or molecules would be a factor in catalytic reactions at surfaces was first spoken of by Langmuir³ although one of us developed experimental proof for it before he was aware of Langmuir's speculation. It is interesting to note that W. C. McC. Lewis⁴ in discussing the radiation hypothesis postulated that the energy necessary to separate the components of the molecule A-B is received in successive quanta and that the components A and B are thus separated in stages. "It seems probable that the spacing of the atoms on the surface of the solid is a fundamental factor, in that such spacing renders possible the fixation of the A and B atoms or groups when these have been partially separated, thereby preventing their mutual return to reform the normal A-B molecule."

The two catalysts showing the most divergent activity in the series of alumina catalysts have been used for the catalysis of a number of reactions. Among these have been the reactions of formic acid,⁵ the dehydration of aceto-amide, of alcohol and of ether, the formation of ethyl acetate from acetic acid and alcohol, of ethylene from ethyl bromide, of

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

⁴ Lewis, *ibid.*, 17, 662 (1922).

⁵ Adkins and Nissen, *THIS JOURNAL*, 45, 807 (1923).

acetone from acetic acid, and of ketones and olefins from a series of 9 esters.

The data obtained in this study have been briefly summarized in the experimental part of this paper. In the following discussions our results are considered in the light of the various theories which have been advanced as to the causation of organic reactions.

Bancroft⁶ in advancing his widely held theory of selective adsorption (of a product of a reaction) to explain reactions induced by catalysts such as alumina and nickel, reached the conclusion that "A catalytic agent tends to produce the system which it adsorbs the most strongly." No exception, of course, can be taken to such a mild statement of the case but if, as the main argument of the article would indicate, one says that a catalytic agent *causes to be produced* the system which it adsorbs the most strongly there is obviously room for differences of opinion. In any form the hypothesis is a corollary of the theoretical speculations of John Ulric Nef and hence is of fundamental importance to the theoretical organic chemist. In the case of the formation of ethylene and water when ethyl alcohol is passed over alumina, Nef would have postulated the preliminary dissociation of the alcohol into ethylidene and water, the former rearranging to give ethylene. According to either Nef or Bancroft the alumina is a catalyst for the reaction because it removes water from the system. If Bancroft's hypothesis is correct, the very meager experimental evidence for Nef's speculations may be greatly augmented. Since the views of Nef and Bancroft on this point are widely held it becomes of great importance that they be either substantiated or confuted.

It is obvious that selective adsorption plays an important role in catalysis. For example, since alumina is a good adsorbent for water, it will probably be a good adsorbent for alcohols, acids, esters, ethers, etc., which contain an oxygen atom. It shows little adsorptive power for hydrogen as compared with nickel and hence the latter will likely be a better adsorbent for hydrocarbons. And since (if we bar the radiation hypothesis) a catalyst cannot act until it is attached to the substance catalyzed, it is apparent that the catalyst should have a high preferential or selective combining power for the substances undergoing reaction. Evidence is here presented that this is sufficient for two reactions, but for the other reactions studied a second important consideration comes into play in determining the extent and direction of the reaction. In these latter cases our evidence is that adsorption is not the determining factor in directing the course of the reactions.

In view of the fact that the alumina catalysts differ so markedly from each other in their ability to form ethylene from ethyl alcohol and in other dehydration reactions the suggestion was made that these catalysts differ

⁶ Bancroft, *J. Phys. Chem.*, **21**, 602 (1917).

because of their ability to remove or absorb water from the system. The alumina from hydrated or colloidal alumina is approximately twice as effective in forming ethylene from ethyl alcohol as the alumina from aluminum *isopropoxide*. But this colloidal alumina is also twice as efficient in forming ethylene from ethyl benzoate, yet this reaction involves no formation of water, as benzoic acid is the second product. Again, the colloidal alumina forms about twice as much carbon monoxide at 360° from ethyl formate as does the *isopropoxide* alumina. In this case ethyl alcohol is the second product, no ethylene being formed. These two catalysts are equally efficient in forming methyl cyanide from acetamide or of acetone from acetic acid, yet both of these reactions involve the elimination of water. *Most striking of all is the fact that a given alumina catalyst causes the formation of the same amount of ethylene from ethyl ether that it does from ethyl alcohol, although there is twice as much water formed from the alcohol as there is from ether.* In order to bring these experimental determinations into accord with the hypothesis of selective adsorption or desorption as to the causation of reactions it seems that an unjustifiable number of subordinate hypotheses must be made.

If the two alumina catalysts under discussion differ from each other in dehydrating power, then there should be a constant difference in their behavior if the dehydration of an homologous series is studied. A long series of experiments indicates that this is not substantiated by the facts and that the difference between the catalysts is a spacial difference rather than a difference in ability to adsorb water.

Ethyl acetate, propionate and butyrate, and propyl and butyl acetate were studied in their reactions with alumina from colloidal alumina and from aluminum *isopropoxide*. This series of esters enabled us to compare the reactions of three homologous alkyl and three homologous acid radicals. The analytical results are to be found in Table I. Certain very significant facts emerge from these data. If we consider the amount of carbon dioxide formed as a measure of the stability of the three acid radicals, it appears that the propionate is more stable than the acetate and the butyrate more stable than the propionate. When we consider the molecular equivalent of olefins formed from the three acetates it is seen that the propyl is much less stable than the ethyl but the butyl is slightly more stable than the ethyl. When an attempt is now made to calculate quantitatively the relative stability of either the acid or alkyl radicals it will be found that these values are not at all the same for the two catalysts. The calculation may be made from the amounts of carbon monoxide formed from the acid radicals when the alkyl radical was the same or from the molecular equivalents of the olefins when the acid radical was the same. For example the butyrate radical is 2.77 times as stable as the acetate for

Catalyst 1 and 2.22 times for Catalyst 2. The propionate radical is 1.75 times as stable as the acetate for Catalyst 1 and 1.33 times for Catalyst 2. However, this calculation involves experimental factors that may be avoided (as repeatedly shown in other papers) by making use of the "ratios" given in the last column of Table I. For example the "ratio" for Catalyst 2 is 2.58 times as great as the ratio for Catalyst 1 in the case of ethyl butyrate, 2.90 times for ethyl propionate and 4.14 times for ethyl acetate. There should be a constant difference in the dehydrating power as noted above, and one catalyst should be as much better than the other in one case as in the other. This is obviously not true. When the calculation is made for the three cases where the alkyl radicals are different and the acid radical is acetate even more marked differences appear. Such differences would be expected if the differential action of the catalysts towards esters is due to spacial differences, because the acid radicals differ not only in chemical properties (which affect their stability) but also in size and shape.

A second conclusion of fundamental importance should be drawn from these experiments. *The relative stability of the members of even an homologous series of compounds cannot be determined by noting the speed of reaction or decomposition because even the relative speeds are a function of the surface at which the reaction takes place.* It is, of course, obvious that the actual speed of a reaction is a function of the surface or of the reagent, but hitherto it has been assumed that *the relative speed* with which the reaction of a series of compounds took place was an index of the relative reactivity of the members of a series. This conclusion has already been verified in other work carried on in this Laboratory which will later be submitted for publication.

On the basis of the theory of selective adsorption, Engelder⁷ expected that the addition of water to alcohol would decrease the proportion of the dehydration reaction. In using titania he found that experiment agreed with theory and that the presence of water reduced the formation of ethylene to a greater extent than it did the formation of ethane. We have recently shown⁵ that for certain concentrations water does not reduce the dehydration reaction of formic acid to a greater extent than it does the dehydrogenation reaction; in fact, we showed that the reverse of this is true. We believe that water cuts down a reaction not because it affects an equilibrium but because it covers a particular part of the surface of a catalyst and hence renders that part inactive.

If such a conception be correct it should be possible to reduce the extent and change the proportion of two possible reactions by the introduction of substances other than water into the reaction chamber. Such experiments would also enable us to determine what sort of substances are able

⁷ Engelder, *J. Phys. Chem.*, **21**, 876 (1917).

to attach themselves to the catalyst. For if a given substance, not a product of the reaction, and not capable of reacting itself, affects the extent of the reaction, it must do so because it has become attached to the catalyst and is thereby reducing the effective surface of the latter. To this end we have studied the effect of water, alcohol, acetic acid, acetone, phenol, phenyl acetate, ethylene and heptane upon the reactions of ethyl acetate, and of ethyl acetate upon the reactions of ethyl formate.

The detailed statement of the experimental results is given in another part of this paper. The general results are as follows. Heptane cuts down the amount of ethyl acetate undergoing reaction to the extent of only a few per cent. and has no effect upon the relative proportions of the reaction. Ethylene, one of the products of the reaction, has *no* effect upon the reactions. Hence, we believe that heptane and ethylene do not attach themselves in any considerable degree to the catalyst in the presence of ethyl acetate. Water, ethyl alcohol and acetic acid all cut down the extent of the reactions, but since the first hydrolyzes the ester and the latter two react at the temperature at which comparisons can be made, the results are not so illuminating. Acetone, phenol and phenyl acetate do not react under the conditions of the experiments and are recovered unchanged. Yet each of these substances very greatly reduces the extent and modifies the relative proportions of the possible reactions of ethyl acetate. Acetone is one of the products of the reaction of ethyl acetate, yet the addition of acetone *increases* the proportion of the reaction which produces it. This result is certainly not in harmony with the idea that the function of the catalyst is the removal of one of the products of a hypothetical equilibrium.

Ethyl acetate does not react at 360°, yet its addition to ethyl formate cuts down very greatly the formation of carbon monoxide. This reduction in the extent of the reaction is not due to the diluting effect of the ethyl acetate because an equal concentration of heptane has a negligible effect upon the formation of carbon monoxide.

We believe that these experiments show conclusively that water, acetone, phenyl acetate, phenol, ethyl alcohol and ethyl acetate *add*, as such, to alumina at temperatures below that at which these substances react. Since water, phenol and ethyl alcohol seem to have an effect very similar to that of the compounds containing a carbonyl group, we are doubtful whether the formation of compounds with alumina involves addition at a double bond.

Sabatier⁸ believed that the decomposition of the esters involved first the formation of metallic salts and alkoxides.⁹ There is no positive evi-

⁸ (a) Sabatier, *Compt. rend.*, 152, 669 (1911). (b) Sabatier and Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., 1922, p. 308.

⁹ It is but fair to Professor Sabatier to state [Ref. 8 (b), p. 57] that he was not dogmatic in his statement of his views, but writes: "As far as I am concerned, this idea of

dence for this view and a great deal of experimental data which are not in accord with it. Briefly summarized, the evidence against Sabatier's hypothesis is as follows.

1. Ethyl acetate and phenyl acetate at temperatures far above their boiling points form compounds with alumina by direct addition and without involving any disruption of the ester.

2. Increase in the amount of free acid and alcohol does not give an increased reaction and gives a different proportion of products.

3. The proportion of products from a given ester depends to a far greater extent upon the physical history of the catalyst than it does upon the nature of the metal in the oxide. Sabatier held that the relative proportions of the products depended upon the relative stability of the salt and the alkoxide. This relationship being a constant, the proportion of the products should be unvarying for any given metallic oxide.

4. In some cases the ester does not give the same products as would the acid or alcohol under the same conditions. For example, ethyl formate gives no carbon dioxide at 360° with alumina from isopropoxide, yet formic acid¹⁰ gives considerable quantities of carbon dioxide under the same conditions. Sabatier's own experimental work supports this point. He observes¹¹ that formic acid over thoria gives a 50% yield of formaldehyde, and later records that ethyl formate gives carbon monoxide and very little formaldehyde. We have duplicated these results.

For these reasons and upon the experimental evidence incompletely referred to in the foregoing discussion of the selective adsorption theory of catalysis, and of the hypothesis of Sabatier, we consider that two facts have been established. 1. Esters attach themselves directly to the catalyst without any preliminary rupture of the molecule. 2. The reactions of the esters are determined by the spacing of the atoms or molecules of the catalyst.

The theory for the catalysis of molecular rearrangements advanced by Arthur Michael taken in conjunction with some of Langmuir's ideas¹² on catalysis seems to offer the most adequate basis for the interpretation of the reactions under consideration. Professor Michael¹³ assumes that temporary unstable intermediate compounds has been the beacon light that has guided all my work in catalysis; its light may, perhaps, be dimmed by the glare of lights as yet unsuspected, which will arise in the better explored field of chemical knowledge." Such a light in the opinion of the author has been lighted by the investigators of the structure of solids and nature of the chemical compounds formed in adsorption. It appears that Sabatier's only error was in his idea of the *nature* of the "temporary unstable intermediate compounds."

¹⁰ Ref. 5, p. 810.

¹¹ Ref. 8 (b), pp. 297, 312.

¹² Langmuir (a), *Trans. Faraday Soc.*, **17**, 607, especially 615-619 and 653-654 (1922); (b) *THIS JOURNAL*, **37**, 1162 (1915); (c) **38**, 1145 (1916); also (Ref. 5).

¹³ Michael, *THIS JOURNAL*, **40**, 1697 (1918); **42**, 798 (1920).

the catalyst unites to form a "polymolecule" with the substance catalyzed (hereafter referred to as the substrate). The "free energy"¹⁴ of the polymolecule is thereby sufficiently increased over that of the substrate to overcome the forces which have hitherto prevented the possible rearrangement. The theory thus stated in terms of energy relationships has never been extensively used but it may be restated in terms of the Lewis-Kossel theory of molecular structure in a way that will satisfy the yearnings of the organic chemist for a structural formulation.

The catalyst unites with the substrate, through some of the electrons of the outer shell of one of the atoms of the molecule. The new arrangement of electrons and atoms is not stable at the temperature of reaction, and a rearrangement of atoms as well as of electrons then takes place to form systems which are more stable. (This may be represented graphically.)

A substance is a catalyst for some reactions (1) if it combines with the substrate, and (2) if this combination involves a shift in the arrangement of the electrons of the substrate such that a rearrangement of atoms may ensue. This conception of a catalyst is adequate for the explanation of some reactions, as for example the dehydration of an amide. We have repeated some of Boehner and Ward's¹⁵ work and agree with them that the catalysts used were about equal in efficiency. We obtained the same yield with three of our alumina catalysts. The amide combines with the catalyst. This combination involves a shifting of electronic configuration such that the nitrile and water may evaporate from the surface upon which the amide was adsorbed, that is, chemically combined.

In order that a substance may be a catalyst for certain other reactions a third condition must be met. There must be an active point or surface on the catalyst at a proper distance from the point at which the first molecule is adsorbed. This may be necessary either in order that reaction between adjacent adsorbed molecules may take place or else in order that this second active point may exert its influence upon an adsorbed molecule, thereby causing it to react in different ways depending upon the distance between the active points.

Langmuir¹⁶ stated that the formation of acetone, ethyl alcohol, ethylene, carbon dioxide and water "from ethyl acetate involves interaction between two molecules which must be adsorbed in adjacent positions in definite geometrical relations to one another." Our experimental work substantiates this statement and gives evidence that the ratio of olefin formation to ketone formation is determined by spacial relationships upon the surface of the catalyst.

¹⁴ This is not identical with free energy as thermodynamically defined.

¹⁵ Boehner and Ward, *THIS JOURNAL*, **38**, 2505 (1916).

¹⁶ Ref. 12 (a), p. 619.

The behavior of acetic acid towards the alumina catalysts points towards still another type of reaction. The four alumina catalysts which show such marked differences for other reactions give almost the same results with acetic acid. That is, the formation of acetone, carbon dioxide and water from acetic acid is almost if not entirely *independent of the spacing of the molecules of the catalyst*. This is a marked contrast to the formation of acetone from ethyl acetate, a reaction which is very sensitive to differences in the spacing of the molecules because reaction apparently takes place between adjacent adsorbed molecules. We interpret the independence of the reaction of acetic acid of surface conditions of the catalyst to mean that acetic acid is attached to the catalyst and that reaction takes place when a molecule of acetic acid impinges or is adsorbed upon the molecule of acetic acid *already* attached to the catalyst.

Sabatier¹⁷ explains the formation of formaldehyde from formic acid in about a 50% yield when the acid is passed over thoria by assuming the formation of carbon dioxide and hydrogen from one molecule of acid and the subsequent reduction of another molecule by hydrogen. We have duplicated Sabatier's results, but since there is absolutely no experimental evidence for the reduction of formic acid over thoria it seems very probable that the formaldehyde is made from the formic acid by exactly the same mechanism as is acetone from acetic acid. The mechanism of the two other reactions of formic acid has been discussed in a previous paper.⁵

The hypothesis that ketones are formed (or formaldehyde from formic acid) by a molecule impinging upon a molecule already attached to the catalyst is supported by some of Sabatier's observations.¹⁸ He observed that mixed ketones of benzoic acid and straight-chain aliphatic acids are easily prepared over thoria, but that it is impossible to prepare a ketone from an aromatic acid alone. We interpret this to mean that the bulk of the benzene ring is so large that a second molecule of an aromatic acid cannot strike the carboxyl group or be adsorbed sufficiently near to the first molecule so that the two can react. However, if a molecule of acetic acid is adsorbed in the surface the methyl group is not sufficiently large to ward off a molecule of benzoic acid from the carboxyl group and hence acetophenone is easily formed. What has been said for the formation of ketones from aromatic acids also holds for the production of ketones from the *iso* or branched-chain acids. The volume of the *iso* group is apparently sufficient to ward off the second molecule necessary for reaction.

A series of experiments was made on the efficiency of three of the alumina catalysts in esterification at 350°, 400° and 465°. At 350° the alumina from aluminum *isopropoxide* was 47% as effective as the alumina from colloidal alumina. At 400° it was 87% as efficient. Although some

¹⁷ Sabatier, *Compt. rend.*, 152, 1213 (1911).

¹⁸ Ref. 8 (b), pp. 303-304. Sabatier, *Compt. rend.*, 159, 217, 219 (1914).

other factors affect the exact value of this relative efficiency, the growing similarity of the activity of two catalysts as a reaction is carried out at a higher and higher temperature, is quite characteristic and has been noted in other cases. This is to be expected because if the less efficient catalyst is as good an adsorbent as the others then there must be many molecules on the surface of this catalyst that fail to react because they are situated *a little* too far apart on the surface of the catalyst. A rather small increase in kinetic energy due to a rise in temperature would increase the amplitude of their vibration sufficiently to allow a great many more to react. (As noted by Reid, with slower rates of passage of the alcohol-acid mixture, yields of esters may be obtained much in excess of the 66% possible in a homogeneous system.) The experiments at 465° are of interest in comparison with the cases where ethyl acetate was passed over the catalyst, and have been discussed.

The alumina from the *isopropoxide* is less than half as efficient as the colloidal alumina for the formation of ethylene from ethyl alcohol at 410°. We were greatly surprised to learn that ether and alcohol are apparently equally stable over alumina and give the same amount of ethylene per hour. There are no apparent differences in the alumina catalysts in their ability to form ethylene from ethyl bromide.

Several other important facts are most economically stated in the tables and need not be discussed at this time.

Experimental Part

The experimental methods were essentially the same, with one exception, as those previously described. This exception has to do with the method of introducing the reacting materials as vapors into the chamber holding the catalyst. Various methods have been proposed and used by Engelder,⁷ Taylor,¹⁹ Adkins,² and Reid.²⁰ Engelder regulated the rate of flow by means of a buret and vaporized by means of a capillary tube held in a hot air-bath. Taylor controlled the rate of flow by distilling with a regulated electric current passing through a wire of known resistance. The distilling flask was surrounded by vapors of the substance distilled, heat losses being thus prevented and rate of distillation easily controlled. Adkins substituted a vacuum jar for the latter purpose. Reid dropped the materials through a calibrated needle valve onto a hot surface. It is difficult to control the rate of flow by Engelder's method. Taylor's and Adkins' methods are not applicable to mixtures. Neither of them is to be recommended for vaporizing low-boiling substances such as ether or high-boiling ones such as phenol and aniline. Reid's device would have to be recalibrated when mixtures of a different viscosity from those orig-

¹⁹ Taylor, *THIS JOURNAL*, 43, 2060 (1921).

²⁰ Reid, New Haven Meeting of the American Chemical Society, 1923.

inally used were to be introduced and would certainly be troublesome if a solid such as acetamide or phenol were to be introduced. We have not found the method of dropping materials upon a hot surface to be a very desirable procedure.

The method designed by Nissen meets all the objections noted above.

Mercury is placed in a dropping funnel the stem of which is attached to a rubber tube. The rubber tube is connected to a rubber stopper bearing a capillary tube. The stopper is inserted into the neck of a tube of the type used for determination of molecular weights by the freezing-point method. The side arm is connected to a 6mm. glass tube bearing a 3-way stopcock and leading through an electrically-heated oil-bath maintained at a proper temperature for the vaporization. The materials to be vaporized are placed in the cryohydric tube, and mercury is allowed to flow through the capillary. The rate of flow is determined by the size of the capillary and the height of the head of mercury.

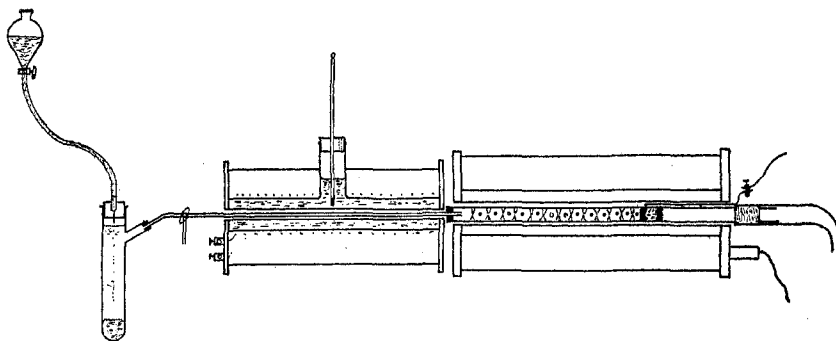


Fig. 1.—Regulator, vaporizer and reaction tube

The cryohydric tube was calibrated so that the rate of introduction of the materials might be closely followed and the rate of flow quickly adjusted. When acetamide was introduced it was kept in a molten condition by immersing the tube in a hot water-bath. The apparatus is illustrated in the figure.²¹ The method and apparatus have given excellent service.

The oil-bath used for the vaporization was constructed from three 10cm. nipples of 2.5 mm. (1 in.) pipe, one T, 2 reducers (25 to 6 mm., or 1 in. to $\frac{1}{4}$ in.) and a 33cm. nipple of 6mm. ($\frac{1}{4}$ in.) pipe. The 10cm. nipples were screwed into the T, the 33cm. nipple of 6mm. pipe was placed within the 25mm. pipe and T and connected to it at each end by the reducers. The larger pipe was covered with asbestos paper and a spiral made from Nichrome wire (40 ohms resistance) was wound around it. The heating unit was then covered with a 25mm. layer of asbestos paper and the whole covered with tape. "Eureka Tempering Oil" was placed within the 25mm. connections so that the 33cm. nipple of 6mm. pipe was surrounded by oil that could be heated and maintained at any desired temperature up to 360°. Parenthetically it may be said that this oil is an excellent one for use in oil-baths. It may be used up to 300° in an ordinary bath or up to 360° or more if loosely covered with an asbestos pad. So far as is known to us the only oils that can compare with it for use in baths are high grade olive oil and completely hydrogenated vegetable oils. The former may be heated to 360° during melting-point determinations.

²¹ See also Ref. 2, and especially Ref. 1, p. 2177.

Reactions of Esters with Alumina.—The analytical results obtained through the study of the reactions of ten esters with alumina are summarized in Table I. The results given for any ester and catalyst represent either the average of a number of closely agreeing results or of runs which have been repeatedly duplicated. The results given are based upon about 90 experiments. In every case 40 to 45 g. of the ester was passed over the catalyst during one hour. The analytical methods, procedure, preparation of catalysts, etc., were those previously described.²

The figures given in the last column of the table were obtained by dividing the amount of ethyl acetate equivalent to the olefin by the amount equivalent to the carbon dioxide. This figure represents the number of molecules of ester that gave an olefin in terms of the number of molecules that gave carbon dioxide and acetone.

Catalysts.—Catalyst 1 was 0.68 g. of alumina from aluminum *isopropoxide* on pumice (total 4 g.). Catalyst 2 was 2.5 g. of hydrated alumina, obtained either by the action of aluminum amalgam on water or from aluminum nitrate and ammonium hydroxide and was in pill form. Catalyst 3 was 2.5 g. of alumina from aluminum *isopropoxide*, in pill form. Catalyst 4 was 2.5 g. of alumina from crystalline aluminum hydroxide and was in pill form.

Catalyst 4 was obtained through the courtesy of Dr. Junius D. Edwards, Assistant Director of Research of the Aluminum Company of America. A sample of the product

TABLE I
REACTIONS OF ESTERS WITH ALUMINA

Catalyst	Temperature °C.	Reacting substance	CO ₂ G.	C _n H _{2n} G.	Acid G.	AcOEt equiv. C _n H _{2n} / AcOEt equiv. CO ₂
1	465	Ethyl butyrate	1.80	1.76	..	0.77
2	465		1.35	3.42	6.0	1.99
1	465	Ethyl propionate	2.85	1.76	1.4	0.49
2	465		2.25	4.00	4.5	1.42
1	465	Propyl acetate	4.50	5.13	1.3	0.60
2	465		3.40	10.9	6.0	1.68
1	465	Butyl acetate	3.65	3.70	1.1	0.29
2	465		2.40	8.80	5.4	1.46
3	465		3.10	3.30	0.5	0.35
1	430	<i>Isopropyl acetate</i>	2.00	8.36	5.5	2.11
1	465		3.90	16.9	10.0	2.23
2	430		0.60	14.4	17.6	1.24
1	490	Ethyl benzoate	.21	3.75	16.1	..
2	490		0.18	6.64	28.4	..
1	490	Phenyl acetate	Nil			
2	465	Acetal	0.4 ^a	6.7
1	465		.6 ^a	3.0
1	360	Ethyl formate	6.9 ^a	0.0
2	360		13.0 ^a	.41
1	465	Ethyl acetate	5.00	2.25	0.8	0.35
2	465		3.00	5.40	5.8	1.45
4	465		3.4	3.25	1.1	0.64

^a Carbon monoxide.

obtained by the Baeyer process was washed free from alkali. In a previous³ paper the product obtained by the action of hydrochloric acid upon a solution of sodium aluminate was considered to be the crystalline hydroxide as indicated by Martin.²² Since that material gave a catalyst showing an "ethylene efficiency" of 1.06 and Catalyst 4 gave the figure 0.64, the two are evidently not identical. It is interesting to note that Catalysts 3 and 4 are very similar in catalytic activity but are the most dissimilar in appearance of all the catalysts we have used. One is very dense and crystalline and the other very fluffy and apparently amorphous. The aluminum hydroxide from which Catalyst 4 was prepared has previously been shown to be definitely crystalline.²³ In part at least it is converted, at the temperature at which we used it, into a crystalline form.

Through the courtesy of Drs. W. B. Dexter and A. St. John of the Union Carbide and Carbon Research Laboratories, the aluminum *isopropoxide* and the hydrated alumina obtained from it (Catalysts 1 and 3) were subjected to an X-ray analysis. They reported that "the hydrated alumina has a very distinct structure, although the lines are very faint and somewhat diffused, indicating crystal grains of the order of 0.0001" (0.000004 mm.) or less. The aluminum *isopropoxide* is also crystalline, the grains being 0.002" (0.00008 mm.) or larger, the structural units probably being molecular as distinguished from ionic units as in sodium chloride." Dr. Fritz Conover, with a Hull apparatus, found some crystalline material in the hydrated alumina from which Catalyst 2 was prepared.

Esterification.—Forty to 45 g. of an equimolecular mixture of ethyl alcohol and acetic acid was passed over the catalyst during one hour. In the absence of a catalyst no gas was formed and not more than a few tenths of a gram of ester was formed at temperatures between 200° and 400°. The results of some fifty experiments upon esterification with alumina are summarized in Table II.

TABLE II
FORMATION OF ETHYL ACETATE

Temp. °C.	Catalyst	Ester G.	CO ₂ G.	C ₂ H ₄ G.	Ratio
350	1	5.2	Nil	Nil	..
400	1	13.8	1.0	Nil	..
465	1	6.0	5.0	1.2	0.18
350	2	11.2	Nil	Nil	..
400	2	15.7	1.0	2.0	1.55
465	2	6.0	2.7	4.1	1.20
350	4	6.0	Nil	Nil	..

The Addition of Various Substances to the Reaction Mixture.—The effect of adding 1 part of acetic acid, ethyl alcohol, heptane, phenyl acetate or acetone to 3 parts of ethyl acetate was determined in a series of some 30 experiments, 40 to 45 g. of the mixture being passed over the catalyst in one hour. The results are summarized below.

Acetic acid over Catalyst 1 increased the carbon dioxide by 24% and decreased the ethylene by 45%, the comparison being made with the results of the standard run as given in Table I. Acetic acid over Catalyst 2 increased the carbon dioxide by 36% and decreased the ethylene by 22%. Phenol over Catalyst 2 decreased the carbon di-

²² Martin, *Mon. Sci.*, [5] 5, 225 (1915).

²³ Milligan, *J. Phys. Chem.*, 26, 247 (1922).

oxide by 40% and the ethylene by 37%. Phenyl acetate over Catalyst 2 decreased the carbon dioxide by 23% and ethylene by 32%. Acetone over Catalyst 1 decreased the carbon dioxide by 10% and the ethylene by 20%. Acetone over Catalyst 2 decreased the carbon dioxide by 15% and the ethylene by 20%. Heptane cut down the reaction to the extent of only 1 to 2% and had no effect upon the proportion of ethylene and carbon dioxide. Ethyl alcohol over Catalyst 1 gave the same amount of ethylene but reduced the carbon dioxide by 40%. Over Catalyst 2 the ethylene was increased by 32% and the carbon dioxide decreased by 25%.

The passage of 10% of water with the ethyl acetate over Catalyst 1 reduced the ethylene by 20% and the carbon dioxide by 28%. Over Catalyst 2 the ethylene was reduced by 50% and the carbon dioxide by 20%. There was an increase in the amount of ester saponified during the experiment; 7 g. of ethylene passed over Catalyst 1 with 40 g. of ethyl acetate had no effect either upon the ratio or amount of products.

As noted in Table I, when 40 g. of ethyl formate was passed over Catalyst 1 at 360° in one hour, 6.9 g. of carbon monoxide was formed. When 30 g. of ethyl formate and 10 g. of ethyl acetate were used, the amount of carbon monoxide was decreased by 26%. When heptane was substituted for the ethyl acetate in the above experiment the amount of carbon monoxide was almost exactly the same as when pure ethyl formate was used.

Dehydration of Acetamide.—Catalyst No. 1, 2, or 3 gave approximately 17 g. of methyl cyanide per hour. In the absence of pulverulent alumina but with glass beads in the reaction tube 8 g. of methyl cyanide was produced.

Ethylene from Ethyl Bromide.—From 2.3 to 2.4 g. of ethylene was formed in half an hour at 465° when 20 g. of ethyl bromide was passed over either Catalyst 1 or 3. It was impossible to use Catalyst 2 because it lost its activity within 3 or 4 minutes.

Ethylene from Ethyl Alcohol and Ethyl Ether.—Forty g. of either alcohol or ether at 410° gave from 5.0 to 5.5 g. of ethylene per hour over Catalyst 1. Either substance gave from 12.0 to 12.5 g. of ethylene per hour over Catalyst 2.

Acetic Acid and Alumina.—Nine to 10.5 g. of carbon dioxide and an equivalent amount of acetone were obtained when 40 g. of acetic acid was passed over Catalyst 1, 2, 3 or 4 at 465°. The amount of reaction was approximately the same for these catalysts. The gas evolved was at least 99% of carbon dioxide.

Conclusions

In the study of the reactions of some fifteen different compounds at the surface of alumina, we have obtained no experimental evidence to support the idea that the function of the catalyst is to remove one member of an equilibrium, or that the catalyst reacts with the substance catalyzed to form compounds such as aluminum acetate or ethoxide. We believe that in every case the substance catalyzed unites chemically with the catalyst with a resultant rearrangement of the electrons of the substrate followed by vaporization of the products. The nature of the rearrangement and subsequent reaction is determined primarily by energy relation-

ships and electronic configuration and in most cases by the spacial configuration of the catalyst.

Esters attach themselves directly to the catalyst without any preliminary rupture of the molecule, and then rearrange and react with adjacent molecules, to give various proportions of acid, ketone, olefin, alcohol, carbon dioxide and water, depending upon the spacing of the atoms of the catalyst. Alcohol and ether are equally stable towards alumina and react by a mechanism similar to that of the esters. Acetic acid attaches itself to the surface of the catalyst and then reacts with a second molecule impinging upon it to give acetone, carbon dioxide and water. Formic acid rearranges, as do the esters, to give either water and carbon monoxide or carbon dioxide and hydrogen. It also gives formaldehyde and carbon dioxide by the mechanism suggested for the formation of acetone from the acetic acid. The relative proportions of these products are determined by the spacing of the atoms upon the surface of the catalyst. Amides must be tied down to some surface before they give nitriles and water, but the character of this surface is relatively unimportant. Alkyl halides probably give olefins and halogen acid by a similar mechanism. It appears that the rate of reaction of these two latter classes of compounds is determined by their rates of adsorption.

Summary²⁴

Two major methods of attack have been used in the investigation reported in this paper. In one series of experiments the behaviors of esters, alcohols, etc., at the surface of various aluminas have been noted. The aluminas differ, we believe, in the spacial relationships of the "active points" of the alumina. In another series of experiments the effect upon the reaction of an ester of introducing water, alcohols, heptane, ethylene, acetic acid, acetone or other esters has been observed. The results of these two types of experimentation have been considered in the light of various theories of catalytic action, and certain conclusions have been drawn.

The *relative* stabilities or reactivities of the members of even an homologous series of compounds cannot be determined by comparing the speeds of reaction or decomposition of the members of the series, because even the relative speeds are a function of the surface at which the reaction takes place.

The formation of ketones from acids, of nitriles from amides, and of olefins from alkyl halides is not affected by modifications in the spacial configuration of the alumina catalysts. The reactions of esters and alcohols are quite sensitive to such modifications.

²⁴ This investigation was subsidized by the Research Committee of the University of Wisconsin, Dean C. S. Slechter, Chairman.

A comparison of the temperature coefficients for the formation of ethyl acetate over two aluminas gives further evidence that the aluminas differ in the space relationships of the molecules or "active points" of the catalyst.

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[CONTRIBUTION FROM THE INSTITUTE FOR ORGANIC CHEMISTRY OF CZECH UNIVERSITY]

PROTOPECTIN AND SOME OTHER CONSTITUENTS OF LEMON PEEL

BY RUDOLPH SUCHARIPA

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Various terms have been used in describing pectin, the jellying principle of fruits, and related substances. There has been much confusion in the literature because workers have not employed the same nomenclature. In this paper three classes of pectic substances will be distinguished, namely, protopectin, free pectin and pectic acid.

The pectic substance occurs in plants in two different forms, only one of which is soluble in water. The soluble or "free pectin" occurs in the fruit and in many other soft places of the plant, both in the juice and in the cell wall. It is located in the cell wall just on the periphery, where two cells meet. This "free pectin" has the highest jelly-making power of the entire pectic group. The water-insoluble class of pectic substances is called "protopectin," a name first proposed by Tschirsch.¹ It occurs only in the cell wall, lying closest to the cellulose layer, nearer the inner part of the wall, under the film of free pectin. It must be understood, however, that the free pectin layer merges into the protopectin layer without a sharp line of division, and in a similiar manner the protopectin merges into the pure cellulose wall inside the cell.

The third class of pectic substances is pectic acid, which is the ultimate product of the hydrolysis of any of the pectic substances. Free pectin is the fully methylated ester of this acid, which is practically insoluble in water.

It has been definitely established by Fellenberg² that protopectin is the methyl ester of pectic acid and not the calcium salt as a number of earlier investigators^{3,4} had thought. This view has been confirmed by the work of D. Haynes⁵ and Devaux.⁶

Julius Wiesner⁷ found that protopectin contains a cellulose radical,

¹ Tschirsch, *Dissertation*, Berne, 1908.

² Fellenberg, *Biochem. Z.*, **85**, 161 (1918).

³ Payen, *Rec. sav. étrang.*, **9**, 148 (1846).

⁴ Chodnew, *Ann.*, **51**, 355 (1844).

⁵ Haynes, *Biochem. J.*, **8**, 553 (1914).

⁶ Devaux, *Lineana*, Bordeaux, 1903.

⁷ Wiesner, *Jahrb. wiss. Bot.*, **1**, 61 (1861).