

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

THE REACTIONS OF FORMIC ACID AT THE SURFACE OF ALUMINA. THE SELECTIVE ACTIVATION OF ALUMINA. II

BY HOMER ADKINS AND BRYNJULV H. NISSEN

Received November 24, 1922

While the causation of certain organic reactions was being studied, the behavior of formic acid at the surface of various types of alumina, titania and thoria was investigated for three reasons. Data on the reactions were necessary for a study of the so-called reductions of acids by means of formic acid.¹ Further information was desired in regard to the selective activation of oxide catalysts.² Evidence was needed as to the validity of the hypothesis of "selective adsorption" as a means of accounting for certain organic reactions.³

Sabatier⁴ made a rather extensive study of the behavior of formic acid towards the usual catalytic agents. He concluded that formic acid might react in three ways, as indicated by the following equations: (1) $\text{HCO}_2\text{H} = \text{CO}_2 + \text{H}_2$; (2) $\text{HCO}_2\text{H} = \text{CO} + \text{H}_2\text{O}$; (3) $2\text{HCO}_2\text{H} = \text{HCHO} + \text{CO}_2 + \text{H}_2\text{O}$. The catalytic metals such as nickel and copper induced Reaction 1 almost exclusively. Titania brought about the second reaction quantitatively, while thoria induced Reactions 2 and 3. Alumina caused about 15 mols. to react according to Equation 2 for every mol. decomposed according to Reaction 1. Hinshelwood, Hartley and Topley⁵ have recently shown that the relative velocities of Reactions 1 and 2 depend upon the temperature and the character of the glass surface at which reaction takes place.

We have investigated the effect of water and temperature upon the reactions induced by various types of alumina, and have arrived at certain conclusions as to the mechanism of the reaction and as to the validity in this case of some of the current theories for catalytic action.

Experimental Part

The apparatus, method of procedure, and preparation of the catalysts were identical with those previously described;² 35 to 45 g. of the formic acid solution was passed over the catalyst in 1 hour. Carbon monoxide was determined both by absorption and combustion. Hydrogen was determined by combustion. The percentage of hydrogen found in the gas agreed quite closely with the carbon dioxide content. Hence Reaction

¹ Sabatier, *Compt. rend.*, **154**, 561 (1912).

² Adkins, *THIS JOURNAL*, **44**, 2175 (1922).

³ Bancroft, *J. Phys. Chem.*, **21**, 573 (1917); *Trans. Am. Electrochem. Soc.*, **37**, 233 (1920).

⁴ Sabatier, *Compt. rend.*, **152**, 1212 (1911).

⁵ Hinshelwood, Hartley and Topley, *Proc. Roy. Soc. (London)*, **100A**, 576 (1922).

3 did not take place to any considerable extent. Carbon dioxide was absorbed in caustic potash solution. A comparison of the contraction in volume when a sample of the gaseous products was exploded, with the contraction observed when the gas had previously been treated with a caustic potash solution, showed that not more than 0.5% of the absorbed gas was formic acid or formaldehyde. The numbers plotted as the ordinates in Figs. 1 and 2 were obtained by dividing the formic acid equivalent of the carbon monoxide by the formic acid equivalent of the dioxide. These figures represent the number of molecules that reacted according to

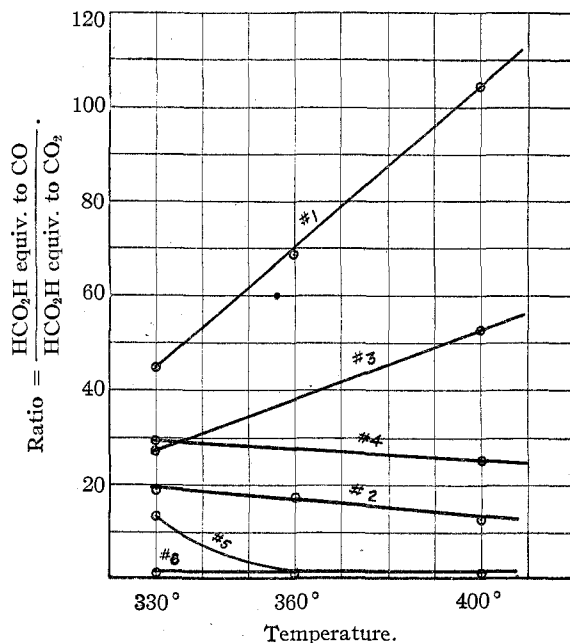


Fig. 1.

Equation 2 while 1 molecule was reacting according to Equation 1. In the discussion, reference is made to this figure rather than to the actual weight of carbon dioxide and monoxide formed under a given set of conditions. This is done, as explained in a previous paper, because the ratio of products is much less sensitive than the actual amounts formed, to the slight and often unavoidable changes or errors in experimentation. Changes in this value in almost every case represent changes in opposite directions of the 2 factors used in calculating it. The ratio of products is plotted against temperature in Fig. 2 for 4 alumina catalysts, glass wool and pumice; 92% formic acid was used in all these experiments. The ratio is plotted against concentration of formic acid (gas phase) in Fig. 1 for 2 alumina catalysts.

The weights in grams of acid decomposed were as follows: by Catalyst 1, Fig. 1, 3.4, 11.0, 11.1, 11.6, 14.2, Fig. 2, 11.6, 19.1, 29.1; by Catalyst 2, Fig. 1, 2.7, 4.0, 5.2, 6.6, 6.4, 7.1, Fig. 2, 6.4, 12.0, 23.7; by Catalyst 3, 10.0,

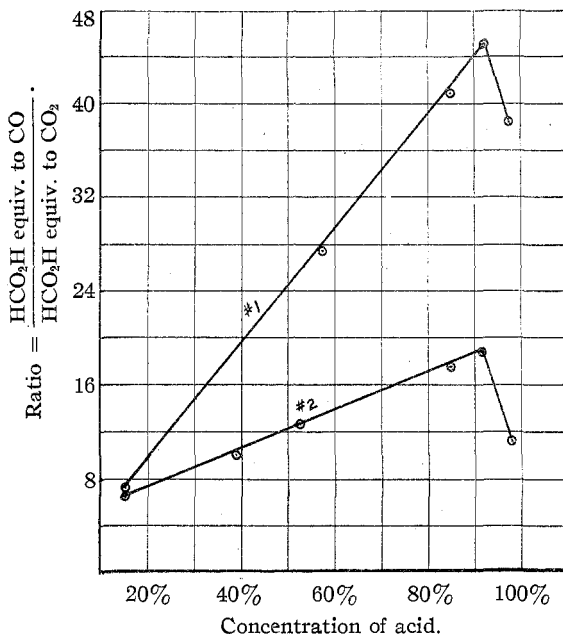


Fig. 2.

34.2; by Catalyst 4, 8.0, 27.6; by Catalyst 5, 0.87, 0.70; by Catalyst 6, 0.56, 2.3, the curves being read from left to right. It should be noted that the data plotted are not the weights of acids decomposed but the ratios of the two reactions.

THE CATALYSTS

No.	G.	Substance
1	2.5	alumina from the reaction of Al-Hg and water
2	0.68	alumina from aluminum isopropoxide on pumice (Total, 4. g.)
3	2.5	alumina from aluminum isopropoxide in pills
4	0.68	alumina from aluminum butoxide on pumice (Total, 4 g.)
5	1	glass wool
6	3	pumice

Interpretation of Results

Three types of alumina catalysts were used: alumina from colloidal alumina, alumina obtained by the action of water vapor upon the solid aluminum isopropoxide, and alumina similarly obtained from aluminum normal butoxide. In a previous paper by one of us, it was shown that these 3 are in a series of 7 alumina catalysts, distinctly different from each other in their behavior towards ethyl acetate. Evidence was presented to show

that these catalysts differed in the distances between the aluminum atoms in the space lattice of the oxide. It was concluded that wider spacing of the atoms is necessary for the formation of acetone from ethyl acetate than for the formation of an olefin.

That the spacing of the aluminum atoms has a very marked effect upon the relative proportions of the two primary reactions (1 and 2) of formic acid is graphically shown in Fig. 1.

The catalyst (1) prepared from colloidal alumina is much less active towards the decarboxylation reaction (1) and much more active towards the dehydration reaction (2) than the alumina (Catalyst 3) prepared from the aluminum *isopropoxide*. The alumina on pumice (Catalyst 2) from the *isopropoxide* is less active for dehydration and more active for decarboxylation than the alumina on pumice (Catalyst 4) from the *normal* butoxide. The action of alumina on pumice is not comparable with that of alumina in pills, for the pumice alone is slightly active towards the formic acid. However, since alumina from the butoxide on pumice gives a higher monoxide ratio than that from the *isopropoxide* on pumice, we are justified in saying that the effectiveness for decarboxylation is greatest for the alumina from the *isopropoxide*, less for the butoxide and least for the colloidal alumina. This order, as well as the relative differences, is similar to that observed for the reactions of ethyl acetate. Selective activation of the alumina was thus very evident for the reactions of formic acid as had been previously demonstrated for the reactions of ethyl acetate.

The dilution of formic acid with water has a marked influence both on the amount of the acid reacting in a given time and in the relative extent of the two reactions (1 and 2). The relation of concentration of acid to the amount and ratio of products was carefully studied with two of the alumina catalysts and the results are plotted in Fig. 1. Increasing the concentration of formic acid from 15% to over 90% caused an approximately linear increase in the proportion of the carbon monoxide for both catalysts, the amount of the increase being very different for the two catalysts. However, when almost pure (98–100%) formic acid was passed over the catalysts there was a much smaller proportion of the carbon monoxide reaction than with less concentrated acids. The rather great proportion of carbon dioxide and hydrogen when 98–100% formic acid was used was not due to decomposition of the acid by the platinum wire used for distillation nor to any other factor connected with the vaporization of almost pure formic acid. Distillations were made during which the conditions of the runs were duplicated except that the acid was not passed over a hot catalyst. There was absolutely no gas formed. It might be noted in this connection that ignited titania decomposes this concentrated acid with the formation of only a trace of carbon dioxide. The greater

proportion of the carbon dioxide reaction from 99% formic acid as compared with 92% acid was characteristic not only of the two catalysts noted in Fig. 1, but also for glass wool, pumice and the other two alumina catalysts.

Hinshelwood, Hartley and Topley⁵ believed that the presence of water had no effect upon the relative ratio of the dehydrating and the dehydrogenating reactions. They obtained the same results in glass with 85% acid as with 96% acid. It so happens that with some alumina catalysts these two concentrations give similar results, but a concentration of acid midway between those mentioned gives a markedly different ratio of monoxide and dioxide. It may be that in the case of a glass surface the effect of water upon the reaction would be much less than with an alumina surface, with its much greater capacity for adsorbing water.

The very considerable relative decrease in the dehydrating reaction when almost pure formic acid was passed over the catalyst as compared with the experiments where 88 to 95% acid was used, is entirely out of harmony with the hypothesis of selective adsorption, for according to this hypothesis the less water there is present in the system, the greater the dehydrating reaction. The ability of water when present in excess of a few per cent. to cut down the dehydrating reaction may be explained as well in terms of the theory noted below as in terms of the selective adsorption hypothesis.

The dependence of the ratio of the two reactions of formic acid upon the spacing of the atoms upon the surface of the catalyst and upon the concentration of the acid in the gas phase over the catalyst is understandable upon the basis of an extension of the Langmuir theory of the mechanism of reactions at surfaces.⁶ Langmuir believes that a molecule is adsorbed through the agency of certain of the electrons of its outer shell. This union of the adsorbed material with the catalyst produces a shifting of the electrons within the molecule of the adsorbed material with possibly a resultant increase or decrease of the ease of reaction of this compound with either a molecule later impinging upon it or with a molecule adsorbed on an adjacent unit of the space lattice of the catalyst.

The theory may be further developed for use in those cases where intramolecular rearrangement takes place at a surface, resulting in either one of two sets of products, as in the case of formic acid and alumina. A catalyst might cause two reactions from one kind of a molecule through either one of two mechanisms. In the one case the molecule might be oriented in one position at certain points on the surface, and in another position at other points. Selective activation of a catalyst would then consist in increasing the number of points on the surface which oriented in one position and decreasing those which oriented in another position. Selective

⁶ *Trans. Faraday Soc.*, **17**, 607 (1922). See especially pp. 615-619 and 653-654. Compare *THIS JOURNAL*, **37**, 1162 (1915); **38**, 1145 (1916).

activation of a catalyst would then be associated with selective adsorption of compounds.⁷ However, in the case of the simple acids and esters which have only one point in the molecule which is strongly active, it seems very probable that all the molecules are oriented in one position. This fact taken in connection with the importance of the spacing of the aluminum atoms in the catalyst points towards the second mechanism as developed below. Suppose that a molecule of formic acid is attached to an aluminum atom or other active point. It is possible for it to rearrange in two ways to give either carbon dioxide and hydrogen or carbon monoxide and water. If the space between the active points in the catalyst is of a certain dimension, then rearrangement may take place to produce one set of products. If it is of a certain other dimension, rearrangement may take place to produce the other set of products.⁸ It is essential then not only that the formic acid be attached to the catalyst but that there be free spaces on adjacent active points of the catalyst.

The addition of water to the formic acid passing over the catalyst results in some water as well as formic acid being adsorbed. The effective surface of the catalyst is thereby reduced. The first few per cent. of water in the acid apparently cuts down the surface for the dehydrogenating reaction more than it does for the dehydrating reaction. More water then reduces the surface for dehydration more rapidly than it does for the dehydrogenation.

A study of Fig. 1 reveals the fact that with alumina from either the colloidal precipitate or from isopropoxide (in pills) the monoxide reaction increases more rapidly with increase of temperature than does the dioxide reaction. However, with alumina on pumice, or pumice alone, or glass wool alone, the carbon dioxide reaction has the higher temperature coefficient. Hinshelwood, Hartley and Topley, in testing the radiation hypothesis as to the causation of reactions, also observed that when formic acid decomposed in glass the carbon dioxide reaction had the higher temperature coefficient. They advanced an hypothesis giving a physical interpretation of the reaction based on this observation. Their hypothesis apparently loses whatever value it may have had in view of the fact that it is now shown that the catalyst determines not only the relative amounts of the two reactions at a given temperature, but also which one has the higher temperature coefficient.

Titania from the ignition of the sulfate decomposed 34.8 g. of formic acid

⁷ This point in connection with a study of adsorption by alumina is being investigated under the direction of Dr. J. H. Mathews by Messrs. O. H. Schunk and M. H. Veazey in the Laboratory of Physical Chemistry of the University of Wisconsin.

⁸ A great deal of experimental evidence for this type of rearrangement in organic compounds which is dependent upon the surface of the catalyst has now been accumulated in a study of the reactions of esters, and will be shortly submitted for publication.

at 330° quantitatively into carbon monoxide and water. Weight for weight, it is over twice as active as the most active alumina catalyst. The activity of thoria from the ignition of the nitrate is between that of titania and that of alumina; the catalyst gave nearly equal proportions of the monoxide and dioxide. The results obtained with titania and thoria are almost identical with those obtained by Sabatier.

Summary⁹

1. Data are presented to show that alumina may be selectively activated towards the two reactions through which formic acid decomposes by modifying the distance between the aluminum atoms.

2. The effect of the amount of water in the gas phase and of the spacing of the atoms in the solid catalyst upon the ratio of the decarboxylation and the dehydration reactions of formic acid is interpreted in terms of an extension of Langmuir's theory of the mechanism of reactions at surfaces.

3. The catalyst determines not only the proportion of the products of the reactions of formic acid but also determines the ratio of the temperature coefficient of the velocity of the two reactions involved.

4. Experimental evidence is presented which is not in accord with the hypothesis of selective adsorption as to the causation of reactions.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF ANIMAL HUSBANDRY, UNIVERSITY OF ILLINOIS]

THE QUANTITATIVE DETERMINATION OF AMINO ACIDS OF FEEDS. II. THE AMINO ACIDS OF LINSEED MEAL, WHEAT BRAN, SOY BEANS AND RED CLOVER HAY

By T. S. HAMILTON, N. UYEL, J. B. BAKER AND H. S. GRINDLEY

Received November 29, 1922

The Van Slyke¹ method for the determination of certain amino acids is limited in its application to pure proteins, solutions of practically pure proteins or protein substances comparatively free from carbohydrates, fiber, fats, etc.^{2,3,4} A method for the direct application of the Van Slyke method to the analysis of feeds has been designed in this Laboratory and applied to the determination of amino acids of oats, corn, cottonseed meal, and alfalfa by Hamilton, Nevens and Grindley.⁵ The amino acids of

⁹ The work described in this paper was supported in part by a grant from the Research Fund of the University of Wisconsin.

¹ Van Slyke, *J. Biol. Chem.*, **10**, 15 (1911); **22**, 281 (1915).

² Gortner, *ibid.*, **26**, 177 (1916). Gortner and Blish, *THIS JOURNAL*, **37**, 1630 (1915).

³ Gortner and Holm, *ibid.*, **39**, 2477, 2736 (1917).

⁴ Grindley and Eckstein, *ibid.*, **38**, 1425 (1916).

⁵ Hamilton, Nevens and Grindley, *J. Biol. Chem.*, **48**, 249 (1921).