[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

STUDIES IN CATALYTIC HYDROGENATION. I. A NEW METHOD OF HYDROGENATION OF VOLATILE SUBSTANCES AND THE RATE OF HYDROGENATION OF ETHYLENE.

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While an enormous amount of work is being done, by a host of investigators, on catalytic hydrogenation, but little of this work has been of a quantitative nature. The present work was undertaken to obtain more information of a quantitative sort on this important reaction. This preliminary paper is intended to put on record some results obtained with a method of hydrogenation somewhat different from those in use, so as to reserve this part of the field for further work.

It has been customary, in hydrogenating volatile substances, to pass a mixture of the gas or vapor and hydrogen over reduced nickel in a long tube. On the other hand, in hydrogenating nonvolatile oils, a common method is to pass hydrogen through the oil containing the catalyst, meanwhile agitating the oil so as to break up the gas bubbles and to keep the catalyst in suspension. The present method is a sort of combination of these two methods in that the volatile substance to be hydrogenated is mixed with hydrogen and this mixture is passed through a nonvolatile inert liquid containing the catalyst, the mixture being thoroughly agitated so as to comminute the gas bubbles and to bring them in intimate contact with the catalyst which is kept in suspension. It is evident that the mixture of hydrogen and reducible gas or vapor may be brought into contact with the nonvolatile oil containing the catalyst in any of the many ways in which hydrogen may be made to act on oils in the various processes that have been proposed for the hydrogenation of fatty acids or their glycerides.

In this preliminary work, ethylene has been the substance studied, though it is intended to extend the work to other gases and to substances sufficiently volatile within the limits of the working temperatures. Ethylene was chosen as it is easy to obtain in pure condition and because its hydrogenation presents the simplest possible case.

The hydrogenation of ethylene has been studied by several, one of the earliest cases of catalytic reduction on record being the work of von Wilde,[1] who exposed a mixture of equal volumes of hydrogen and ethylene to the action of platinum black in an eudiometer and obtained a quantitative yield of ethane. Sabatier and Senderens[2] passed a similar mixture over reduced nickel and found the union to be complete.

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[1] *Ber.*, **7**, 353 (1874).

[2] *Compt. rend.*, **124**, 1358 (1897).

Experimental.

Preparation of the Catalyst.—One hundred grams of infusorial earth were treated with a solution of 50 g. nickel nitrate, $Ni(NO_3)_2.6H_2O$, in about 150 cc. water, and the resulting moist mass added to a strong water solution of 60 g. sodium carbonate, $Na_2CO_3.10H_2O$, to precipitate the nickel as carbonate. The product was well washed and dried and the nickel carbonate reduced by heating, in a glass tube, just below red heat, in a current of pure dry hydrogen till no more water was formed, and cooled in a current of pure dry carbon dioxide. In order to standardize the catalyst, its activity was tried with cottonseed oil, 70 g. of the oil and 1.0 g. of the catalyst being treated with pure dry hydrogen at 180° in the apparatus described in the preceding communication. The iodine number of the oil was lowered, in 60 minutes treatment, from 113.7 to 44.6. Experiment showed that the catalyst did not deteriorate appreciably during the time that each portion of it was in use.

Temperature.—In all of the experiments, the temperature was maintained at $180° \pm 1°$ by immersing the bulb of the reaction flask in an oil bath, the temperature of which was maintained constant by an oil thermostat with mercury contacts, controlling a gas regulator essentially the same as that previously reported from this laboratory.[1]

Materials.—The ethylene was made according to method of Senderens[2] and washed with sodium hydroxide solution. The hydrogen was from zinc and acid and was washed with alkaline potassium permanganate. As an inert medium, in which to suspend the catalyst, melted paraffin was used.

Procedure.—The gas mixtures were prepared in gasometers, holding about 24 l., which were provided with an arrangement for maintaining nearly constant pressure. The same lot of the mixture was used for the whole series of experiments on any one proportion. Each mixture was analyzed for ethylene by the usual method with fuming sulfuric acid. The mixture of gases was run through concentrated sulfuric to dry it and then into the reaction flask which contained, in each experiment, 1.0 g. of the catalyst and 70 g. of the paraffin. The stirrer was run at 3300 to 3500 r. p. m. In each case, time was allowed for the displacement of air from the apparatus and for the hot paraffin to come to equilibrium with the ethylene, hydrogen and ethane passing through it. The attainment of this equilibrium was shown by constancy in the analysis of successive samples of the issuing gases. The amount of ethane in the product, which is the same as the percentage of reduction of the ethylene, was calculated by the following formula, in which E_1 is the percentage of ethylene in the original mixture and E_2 is the percentage of ethylene in the

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[1] *Am. Chem. J.*, 41, 148 (1909).

[2] *Compt. rend.*, 151, 392 (1911).

products of the reaction. Ethane $= \frac{100E_1 - 100E_2}{100 - E_2}$. Fresh lots of catalyst and of paraffin were used for each 24 l. of mixture.

The rate of gas flow and the composition of the original mixture are the only variables studied in the present work. The results are given in tabular form and are reproduced in curves.

RESULTS.

% Ethylene in org. mixture.	Rate of flow cc. per min.	Ethane %.	Reduction %.	Gas handled cc. per min.	% Ethylene in org. mixture.	Rate of flow cc. per min.	Ethane %.	Reduction %.	Gas handled cc. per min.
10.0	10	6.8	68	1.4	32.5	25	20.4	63	10.2
	25	5.1	51	2.5		50	13.4	41	13.4
	50	3.9	39	3.9		100	9.6	30	19.2
	100	2.7	27	5.4		200	4.8	15	19.2
	200	2.1	21	8.4	49.8	10	34.1	69	6.8
20.0	10	14.1	70	1.4		25	31.4	63	15.7
	25	9.4	47	5.9		50	21.1	42	21.1
	50	6.4	32	6.4		100	17.0	34	34.0
	100	5.1	25	10.2					
	200	3.0	15	12.0					

Discussion of Results.

The results are by no means as regular as could be wished, and some are evidently out of relation to the others. They are not to be considered as final. The irregularities may depend on factors not as yet known or controlled. In Fig. 1 the percentage of the ethylene reduced is plotted against the rate of flow. The interesting result is that, for all of the mixtures, about 70% of the ethylene is reduced when the rate of flow is 10 cc. per minute. All of the results for the 10% mixture are regular and as would be expected. Those for mixtures containing higher percentages of ethylene are by no means so regular and the curves are in

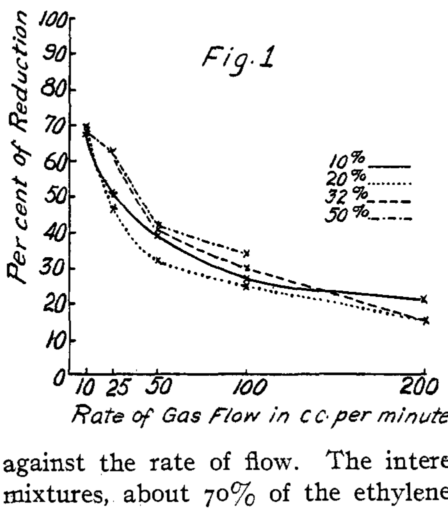
Fig. 1

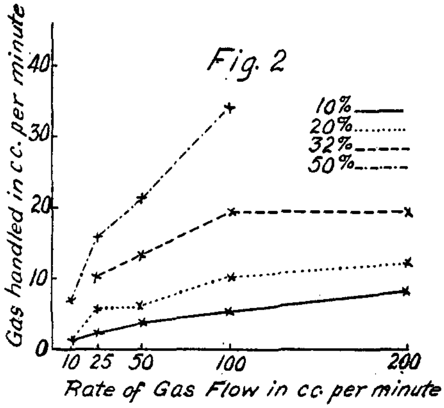
Fig. 2

unexpected relations to each other. Doubtless the determining factor is solubility. The reaction is probably taking place between the ethylene and the hydrogen that are dissolved in the paraffin. The mass law then holds for this solution and not for the gases that are not in solution. When the passage of the gas mixture is rapid, the gases are swept through before equilibrium can be established between the gas mixture and the solution.

In Fig. 2 the volume, in cc., of gases made to combine, per minute, is plotted against the rate of flow. As was to be expected, this amount increases with the amount of the gas mixture that is exposed to the action of the catalyst. The results for the different mixtures are in the expected order, those for the rate of 100 cc. per minute being the most instructive. Under these circumstances, in the 50% mixture, 17 cc. of hydrogen is made to combine with 17 cc. of ethylene in 1 minute. Since the 1 g. of the catalyst, as prepared, cannot contain more than 0.1 g. nickel, the volume of this, considered as Ni, would be about 0.01 cc. or less. Hence the catalyst induces the reaction in 3400 times its own volume of the gas mixture in 1 minute. In the experiment with cottonseed oil, given above, the same amount of nickel caused the absorption of 4230 cc. of hydrogen or 423,000 times its own volume of hydrogen in 60 minutes, or 7000 times its own volume in each minute. These volumes are calculated for a temperature of 0° and would be 67% greater at 180°, at which the action really took place. The amount of hydrogen caused to combine with the oil is several times as great as the amount combined with the ethylene, which is as would be anticipated, as the concentration of the ethylene in the paraffin is probably much smaller than the concentration of the oleine in the oil, and the partial pressure of the hydrogen in the mixture is only half so great as in the pure hydrogen. However, the results are of the same order of magnitude.

Further work is anticipated, and it is desired to reserve the study of the various factors influencing the rate of hydrogenation in gaseous mixture as well as the extension of the method to other unsaturated gases and vapors.

Conclusions.

1. It has been shown that hydrogen and ethylene combine readily when a mixture of the two gases is passed through an indifferent oil in which a nickel catalyst is kept in suspension. These experiments indicate a new method of hydrogenating volatile substances.

2. Some quantitative measurements have been made on the rates of combination of ethylene and hydrogen under the influence of a nickel catalyst under different conditions.

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