

2. With dil. nitric acid the tetramine was hydrolyzed and neither the trinitramine nor the addition compound was formed. With intermediate concentrations of acid, the nitramine, the addition product and the products of hydrolysis were obtained in amounts varying with the temperature, time of nitration and other factors.

PICATINNY ARSENAL  
DOVER, NEW JERSEY

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]  
**THE HYDROGENATION OF ETHYLENE IN THE PRESENCE OF  
METALLIC CALCIUM**

BY ROBERT N. PEASE AND LELAND STEWART

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The intermediate-compound theory of catalysis suggests that substances which form moderately stable hydrides should be suitable hydrogenation catalysts. As no record could be found of an experimental test of this point, an investigation of the combination of ethylene and hydrogen in presence of metallic calcium was undertaken.

We anticipated some difficulty in obtaining a free metallic surface of calcium, or of any other alkali or alkaline earth metal forming a hydride, and it occurred to us that perhaps the liquid sodium-potassium alloy, through which we could bubble the reactants, thus creating a fresh surface for each element of gas volume, would give results. When such an experiment was tried, however, no action whatever was observed at 300°. Some further consideration then brought forth the suggestion that, owing to the much greater thermal expansion of the metal as compared to the oxide or other compound with which the metal might be coated, the application of heat should develop crevices in the coating through which the reactants could gain access to the free metal surface. We were thus encouraged to carry out the experiments with calcium.

Metallic calcium in the form of turnings was washed with ether<sup>1</sup> to remove a film of grease, and sealed into a glass bulb. The latter was connected by a glass capillary to a manometer, gas buret and Töpler pump by means of suitable stopcocks. The apparatus and general method were the same as in previous work on the ethylene-hydrogen reaction.<sup>2</sup> Since a pressure decrease might have been due to absorption of ethylene or hydrogen rather than to reaction, preparations were made to analyze the gas pumped from the catalyst bulb.

<sup>1</sup> The ether used had not been previously dried and a noticeable evolution of gas, presumably hydrogen, took place during the washing. It is not impossible that the consequent pitting of the metal surface was partially responsible for its subsequent activity.

<sup>2</sup> Pease, *THIS JOURNAL*, 45, 1196 (1923).

### Results

A preliminary run was carried out at 200° with a 50% ethylene-hydrogen mixture. A rapid pressure decrease to nearly 0.5 atmosphere at an initial rate of about 50 mm. of mercury per minute was noted. The residual gas was analyzed for ethylene only and found to contain 5%. It seems probable that reaction had taken place, although the possibility that ethylene was absorbed by the calcium is not excluded.

Although it is generally reported that calcium hydride is formed only at red heat, it was thought that some action, perhaps adsorption, would appear at 200°. Experiment proved that our calcium took up hydrogen almost instantaneously and in large volume at this temperature. In all, 7.60 liters (N. T. P.) was absorbed by the sample of 18.73 g. of calcium. This would correspond to the conversion of 72% of the calcium to calcium hydride, but undoubtedly a part at least of the hydrogen was simply held in solution. The chief evidence for the latter statement was obtained from approximate determinations of the dissociation pressure of the hydride, using the Töpler pump as a MacLeod gage. These gave a value of 0.08 mm. at 200° for the sample mentioned above after long continued pumping. Another sample containing only  $\frac{1}{10}$  as much hydrogen gave a pressure of 0.01 mm. Such variability in the dissociation pressure indicates the presence of a solid phase of varying composition. A rough extrapolation of the data of Kraus and Hurd<sup>3</sup> yields a value of  $10^{-5}$  mm. at 200° for the true dissociation pressure.

The catalyst was considerably more active after saturation with hydrogen. A 50% ethylene-hydrogen mixture reacted at an initial rate of about 150 mm. of mercury per minute at 200°. Analysis of the residual gas from one experiment proved the presence of 92.7% of ethane, 3.8% of ethylene, 3.5% of hydrogen. There was thus no doubt that reaction had actually taken place.

The intermediate-compound theory would require that calcium hydride should hydrogenate ethylene directly. To determine whether this is the case, pure ethylene was admitted to the catalyst bulb and, after standing, was withdrawn and analyzed. It was found that ethane was formed, but at a very low rate as compared with that of the catalyzed reaction. At the same time there was a marked decrease of pressure with the disappearance of a part of the ethylene. Thus, in one run of four hours, the pressure dropped 300 mm. from atmospheric, while out of 19 cc. of ethylene introduced, 7 cc. was not recovered. Of the remainder (12 cc.), 8 cc. was converted to ethane. Two cc. of hydrogen was also found in the gas pumped off. In another run of 40 hours, 10 cc. of ethylene was introduced, of which about half disappeared, while 90% of the remainder (4.5 cc.) was converted to ethane. The recovered gases again contained hydrogen.

<sup>3</sup> Kraus and Hurd, *THIS JOURNAL*, **45**, 2559 (1923).

An attempt was made to "burn off" the absorbed ethylene with hydrogen. The bulb was filled with hydrogen and left overnight at 200°. Out of 19 cc. of hydrogen run in, 15 cc. was recovered. This gas contained a small amount of hydrocarbon which behaved more like methane than ethane on analysis and did not exceed 1 cc. in amount. This is to be compared with approximately 28 cc. of ethylene which was absorbed by the calcium in the course of the experiments. No ethylene was recovered.

With a view to working out the kinetics of the reaction, several experiments were carried out at 25° and 100°. The results were rather unsatis-

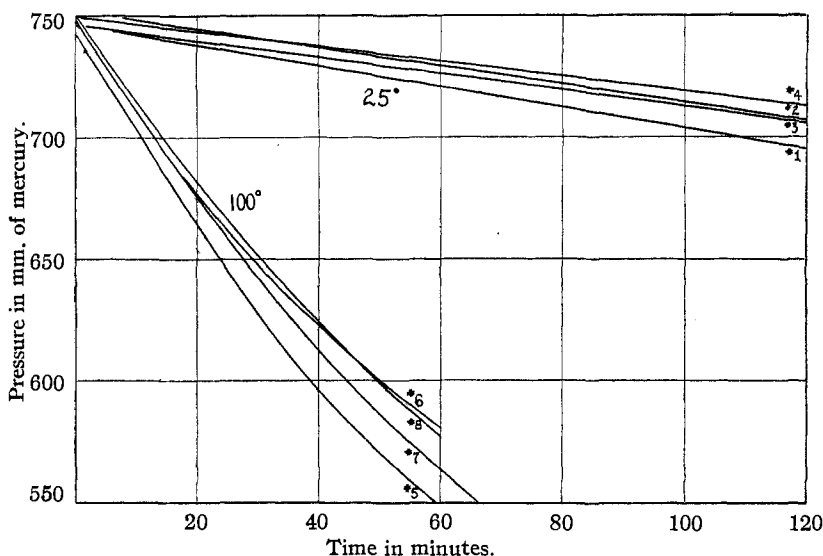


Fig. 1.—Ethylene-hydrogen reaction in the presence of calcium saturated with hydrogen.

At 25°.	At 100°.
1. 1C <sub>2</sub> H <sub>4</sub> : 1H <sub>2</sub> .	5. 1C <sub>2</sub> H <sub>4</sub> : 1H <sub>2</sub> .
2. 2C <sub>2</sub> H <sub>4</sub> : 1H <sub>2</sub> .	6. 2C <sub>2</sub> H <sub>4</sub> : 1H <sub>2</sub> .
3. 1C <sub>2</sub> H <sub>4</sub> : 2H <sub>2</sub> .	7. 1C <sub>2</sub> H <sub>4</sub> : 2H <sub>2</sub> .
4. 1C <sub>2</sub> H <sub>4</sub> : 1H <sub>2</sub> .	8. 1C <sub>2</sub> H <sub>4</sub> : 1H <sub>2</sub> .

factory due to a steady decrease in the activity of the catalyst. In spite of this, the fact that the reaction is more nearly of zero order seems to be established. Curves for the four best consecutive runs at 25° and at 100° with 1:1, 2:1, 1:2 mixtures of ethylene and hydrogen are shown in Fig. 1. It will be noted that the curves are nearly straight lines and are nearly parallel. A set of straight parallel lines would correspond to a zero-order reaction.

#### Discussion

When this research was undertaken, it was felt that a positive result would favor the hypothesis that the function of a metal hydrogenation

catalyst is to convert hydrogen molecules into negative hydrogen ions, the form in which hydrogen is present when in combination with calcium. It is a characteristic property of metals to give up electrons to atoms capable of forming negative ions and the activation of hydrogen by metals appeared to be explicable by this mechanism. This would involve the formation of surface hydride and its subsequent "reduction." However, we have found that in the presence of calcium or calcium hydride the catalytic reaction takes place very much more rapidly than does the reaction between calcium hydride and ethylene, which leads to the conclusion that the latter reaction is not one of the steps in the catalytic reaction. It follows, therefore, that even with calcium as catalyst we are still dealing with an action of the contact type and no evidence is forthcoming that the hydride-forming property of the catalyst is that which is responsible for its catalytic activity.

It is not wholly clear how the mechanism of the reaction is to be formulated. The experimental facts to be considered are, first, that the reaction rate is remarkably insensitive to changes in the partial pressures of the reactants and, second, that when either ethylene or hydrogen is given time to condense on the calcium, the resulting complex is relatively inactive toward the other gas. The first of these facts indicates an approach to saturation of the catalyst surface within the pressure range investigated. In addition it would seem necessary to postulate that molecules of either ethylene or hydrogen must be activated by contact with the surface, but that both need not be. Since neither gas is reactive when actually combined with the surface, it is clear that only contact is necessary or desirable. The molecules are perhaps reactive only when in process of condensation on the calcium.

### Summary

It has been shown that metallic calcium or calcium hydride will catalyze the combination of ethylene and hydrogen, but that it is very doubtful whether the reaction of ethylene with the hydride is one stage in the reaction.

UNIVERSITY, VIRGINIA