

version to ether of about 85%. The corresponding equilibrium constant is 8.0.

4. It has been found that absolute purity of the catalyst is essential. Impurities may be more quickly and completely removed by alternately heating to 350° and washing again.

5. Heating the catalyst to about 400° but not higher, in drying, was found to give the most active product.

6. The catalysts prepared as described retain their activity, unimpaired, after long use.

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## THE NITRATION OF HEXAMETHYLENETETRAMINE<sup>1,2</sup>

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### Introduction

Hexamethylenetetramine possessing weakly basic properties reacts with acids to form salts. Thus the phenate,<sup>3</sup> citrate,<sup>4</sup> camphorate<sup>5</sup> and perchlorate<sup>6</sup> of the base have been prepared and patented for use as pharmaceutical compounds. Ischidzu and Inouye<sup>7</sup> reported that the tetramine is decomposed by hydrochloric, sulfuric, acetic, succinic and salicylic acids to give chiefly formaldehyde, ammonia, carbon dioxide and methylamine. The relative amounts of the different decomposition products formed depend on the concentration of the acid used, the temperature and the duration of the action.

With regard to the action of nitric acid on hexamethylenetetramine, Henning<sup>8</sup> has reported that the amine does not lend itself to the usual methods of nitration, as it is decomposed into formaldehyde and ammonia. However, he described a method for preparing a nitro compound of the formula  $C_3H_6O_6N_6$ , which involves treating an aqueous solution of hexamethylenetetramine with nitric acid to obtain hexamethylenetetramine nitrate and then adding the dried nitrate in small portions to nitric acid, d. 1.52, cooled to  $-5^\circ$ ; after the mixture is allowed to stand in the cold for half an hour and is then poured into ice water, the nitro compound separates in the form of colorless crystals. These crystals are said to melt

<sup>1</sup> This paper is prepared from a thesis submitted by G. C. Hale to the Faculty of the Graduate School of Indiana University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Published by permission of the Chief of Ordnance.

<sup>3</sup> E. Defrance, *J. Pharm. Belg.*, **3**, 605 (1921).

<sup>4</sup> Brit. pat. 26,160, Nov. 22, 1911.

<sup>5</sup> U. S. pat. 1,064,227, June 10, 1913.

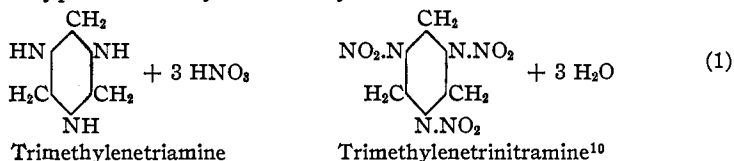
<sup>6</sup> Ger. pat. 292,284, July 27, 1915.

<sup>7</sup> Ischidzu and Inouye, *Chem. Centr.*, **77**, 1087 (1906).

<sup>8</sup> Henning, Ger. pat. 104,280, June 14, 1899.

at 200°, to be insoluble in water, soluble with difficulty in hot alcohol and readily soluble in acetone. The composition of this previously unknown compound is given by Henning in his patent as follows: N, 38.34%; C, 16.15%; H, 2.81%; O, 42.40%. These values agree fairly closely with the calculated values for  $C_3H_6O_6N_6$ . No suggestion as to the probable structure of the compound was offered.

More recently Herz<sup>9</sup> has covered by patent an explosive compound, cyclotrimethylenetrinitramine, which he has found can be prepared by treating hexamethylenetetramine directly with concd. nitric acid. This compound was stated by Herz to be derived like hexamethylenetetramine from the hypothetical cyclotrimethylenetriamine.



The nitration process described comprises briefly the addition of the tetramine, in small portions, during stirring, to nitric acid, d. 1.52, at a temperature of 20–30°. When all of the amine is in solution the mixture is heated slowly to 55° and allowed to stand for a few minutes. The mass is then cooled to about 20° and the nitramine precipitated by the gradual addition of water. The compound is described as a white, crystalline powder, insoluble in water, slightly soluble in hot alcohol and readily soluble in acetone; m. p., 200°.

From the composition and chemical properties given, it is apparent that the nitro compound described by Henning is the same as that patented by Herz. But the method of preparing the compound as described by Herz is different from that patented by Henning and is incompatible with Henning's statement that hexamethylenetetramine cannot be nitrated directly to yield a nitro compound because of decomposition of the base into formaldehyde and ammonia. In an attempt to carry out this nitration in accordance with the procedure given by Herz it was found that the reaction was so rapid that violent oxidation occurred which resulted in either a fume-off or a yield of only 2–3% of the nitration product.

The uncertainty which thus seemed to exist regarding the reaction between nitric acid and hexamethylenetetramine led to the investigation described in the remainder of this paper.

### Experimental Part

An attempt was made to prepare trimethylenetrinitramine by further nitration of hexamethylenetetramine nitrate, as it was desired to compare

<sup>9</sup> Herz, U. S. pat. 1,402,693; Jan. 3, 1922.

<sup>10</sup> Satisfactory proof that this is the correct formula for the compound described by Herz has not been given.

results from this method with those obtained by the direct nitration of the tetramine.

The hexamethylenetetramine used for the nitration was of U. S. P. grade, m. p., 280° (corr.), except in a few cases, which will be indicated, where the material was further purified for special reasons.

**Preparation of Hexamethylenetetramine Nitrate.**—A solution of 50 g. of the tetramine in 150 cc. of water was cooled to 0°, and to it c. p. nitric acid (d., 1.42) cooled to 0° was added gradually. The nitrate was precipitated immediately in the form of small, white crystals which were separated by filtering the solution through glass wool. They were washed quickly with 50% ethyl alcohol previously cooled to 0°, and then given additional washings with alcohol and finally with ether. The mass was then dried with warm air; average yield, 78.2 g.

The compound melted sharply at 165°. It was readily soluble in water but the solution decomposed on standing, giving off formaldehyde; the crystals were insoluble in alcohol, ether, chloroform, acetone and carbon tetrachloride.

The aqueous solution reacted strongly acid. By titrating samples in solution the compound was found to contain 47.22% of nitric acid. This agrees closely with the nitric acid content required for an addition compound containing 1 mol. of hexamethylenetetramine and 2 mols. of nitric acid, that is, 47.34%. The compound did not react with phenylhydrazine, whereas nitron gave a heavy precipitate of nitron nitrate.

The structural formula for this compound is, therefore,  $C_6H_{12}N_4 \cdot 2HNO_3$ . On this basis the yield of 78.2 g., as noted above, corresponds to a calculated yield of 82.3%.

**Nitration of Hexamethylenetetramine Nitrate.**—Table I gives the results of several representative nitrations in which nitric acid at various concentrations and at different temperatures was used.

The nitrations were carried out by adding 5 g. of the dried hexamethylenetetramine nitrate, obtained as described above, in small portions to the c. p. acid contained in a 100cc. beaker. The acid was stirred only gently during the addition of the salt, as it was soon found that vigorous agitation caused a hasty reaction which tended toward a violent fuming of the mass. During the addition of the nitrate and for a short time after, the solution showed slight effervescence and the odor of formaldehyde was evident. As soon as the solution became quiet the charge was poured slowly into ice water, whereupon a white crystalline compound separated.

The mass was filtered through glass wool, washed repeatedly with water until free

TABLE I  
NITRATION OF HEXAMETHYLENETETRAMINE NITRATE  
25 g. of nitric acid was used in each experiment.

Expt.	Concn. of HNO <sub>3</sub> , %	Temp. ° C.	Time Mins.	Yield of C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> , %
1	95	-5	80	43
2	95	30	45	49
3	95	55	10 <sup>a</sup>	10
4	90	30	60	40
5	90	60	20	48
6	85	30	60	34
7	85	60	20	40
8	80	30	60	None
9	80	60	20	None

<sup>a</sup> The reaction became violent, and the charge was drowned as quickly as possible.

from acid and then dried at 100°. The material was insoluble in water and alcohol but readily soluble in glacial acetic acid and acetone. After one recrystallization from acetone the crystals melted at 202° (corr.). The nitrogen content as determined by the Dumas method was 37.65%; that calculated for trimethylenetrinitramine is 37.84%. The temperature required for spontaneous explosion was 290°. These tests were sufficient to prove that the compound was the same as that described by Henning and Herz.

The best yields were obtained with the higher concentrations, 90 and 95%; the 80% acid appeared to decompose the nitrate without further nitration, since in Expt. 8 formaldehyde was continually evolved during the hour that the charge was allowed to stand.

**Nitration of Hexamethylenetetramine.**—The hexamethylenetetramine used for the direct nitrations was from the same lot of U. S. P. material as that from which the hexamethylenetetramine nitrate was prepared. The acids were C. P.

The well-dried tetramine was added in small portions to the acid contained in an ice-cooled glass beaker, and during the process of addition the acid was stirred continuously but only slowly. After the nitration was completed the acid solution was poured into four times its volume of cold water and the liquid filtered through glass wool. The product was then washed with cold water until free from acid and dried at 100° to constant weight.

Yields were calculated on the basis of 1 mole of trimethylenetrinitramine,  $C_3H_6O_6N_6$  (222 g.), being produced from 1 mole of hexamethylenetetramine  $C_6H_{12}N_4$  (140 g.), in accordance with the following reaction.



This required 15.85 g. of the trinitramine from the 10 g. of tetramine used in each experiment.

In a few preliminary tests 70% nitric acid was used at fairly high temperatures. Nitration to the trinitramine apparently did not occur at all at 70°, for no precipitate was obtained upon drowning the solution in water. At 90° oxidation of the tetramine resulted, the charge beginning to fume so violently that it was poured into water to avoid possible accident.

Table II gives the results of a series of experiments in which nitric acid of 92 and 100% concentration was used. Expt. 10 was carried out according to the procedure outlined in U. S. patent 1,402,693. The result, together with that from Expt. 11, which are representative of those from a number of similar nitrations, indicated quite definitely that the conditions of the experiments were conducive to oxidation rather than nitration. The fume-offs noted occurred very suddenly, only a few seconds elapsing after the first red fumes were noticed until the entire charge had escaped from the beaker. Upon resorting to 92% nitric acid better results were obtained immediately.

The data given under Expts. 12 to 22 show quite conclusively that in nitrating with 92% acid no better yields are obtained by allowing the charge to stand longer than 20 minutes after the amine has been added

TABLE II

## NITRATION OF HEXAMETHYLENETETRAMINE

The conc. of nitric acid was 100% in Expts. 10 and 11 and 92%<sup>b</sup> in all other experiments.

Expt.	Wt. of HNO <sub>3</sub> , g.	Wt. of C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> , g.	Max. temp. during nitration, ° C.	Time to add amine Min.	Time held before drowning, min.	Yield of C <sub>6</sub> H <sub>8</sub> O <sub>2</sub> N <sub>4</sub> , %
10	70	10	30 <sup>a</sup>	10	15	2.2
11	75	10	10	30	5	fumed off
12	115	10	20	8	15	41
13	115	10	20	20	15	64
14	115	10	30	15	40	38
15	115	10	18	30	55	57
16	330	30	25	15	60	62
17	330	30	30	10	15	59
18	450	30	27	15	20	60
19	450	30	25	15	60	60
20	450	30	25	15	120	62
21	550	50	30	15	20	63
22	550	50	30 <sup>c</sup>	15	20 <sup>c</sup>	68

<sup>a</sup> The temperature was raised to 50–60° during the interval before drowning.

<sup>b</sup> This acid, although of C. P. grade, contained about 0.7% of NO<sub>2</sub>.

<sup>c</sup> The charge was cooled to 0° during the interval before drowning.

to the acid; that is, the reaction is very rapid. It is also shown that an increase of 4–5% in yield is effected by cooling the charge to a low temperature as soon as the tetramine is in solution; this last point would seem to indicate that a side reaction also occurs at the temperatures used for the nitration, that is, 25–30°, and that this side reaction is inhibited by low temperature to greater extent than is the nitration. This point is discussed later.

The experiments indicate further that the use of 11 parts of nitric acid to 1 part of the amine gives as good a yield of the nitramine as when 15 parts of acid are used, and that 15 minutes is about the minimum time that should be taken for the addition of the given amount of tetramine to the acid.

Since the above results indicated the difficulty of obtaining a yield of the nitramine greater than 66–68%, an effort was made to account for the loss; it was thought desirable to determine whether the remainder of the hexamethylenetetramine was being oxidized or otherwise converted into products other than the trinitramine.

To this end, a nitration was carried out in a closed system in order that the gaseous products could be collected. The acid was placed in a small balloon flask provided with three openings. A thermometer was inserted into the acid through a tightly fitting stopper in the central opening of the flask. An outlet tube passed through the stopper of a second opening, and led to two wash bottles containing distilled water, thence to a tube containing heated copper oxide, and finally to two wash bottles containing lime water; the latter bottles were connected to the vacuum line. The

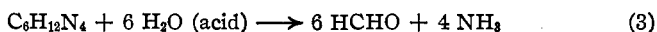
third opening of the flask was fitted with a stopper through which passed a tube leading to a tower of soda lime; the air was drawn through this tower before entering the nitrating flask. The flask was inserted in an ice-bath. The hexamethylenetetramine was added in small portions to the acid through a second hole in the stopper holding the thermometer.

The water in the wash bottles absorbed any formaldehyde liberated from the nitrating acid while the tube of heated copper oxide served to oxidize any carbon monoxide to carbon dioxide which was then precipitated as calcium carbonate in the bottles containing lime water. Any ammonia or methylamine produced in the reaction was retained as the nitrate in the nitrating acid.

Prior to the analysis of the products the drowned nitration acid was added to the water used to absorb the formaldehyde and the whole diluted to definite volume. The formaldehyde was determined by oxidation to formic acid with hydrogen peroxide in an excess of 0.33 *N* sodium hydroxide solution and back titration with 0.33 *N* sulfuric acid. The carbon monoxide and carbon dioxide were collected as calcium carbonate, which was collected on a Gooch crucible and weighed.

The products from a nitration of 10 g. of hexamethylenetetramine under the same conditions as in Expt. 21 above were found to be as follows: trimethylenetrinitramine, 8.83 g.; formaldehyde, 7.45 g.; ammonia, 1.16 g.; carbon dioxide, trace; methylamine, none.

It was assumed that the nitration proceeded according to Equation 2. According to this equation only 5.57 g. of hexamethylenetetramine is required to produce the 8.83 g. of trimethylenetetramine obtained. This amount would yield 3.589 g. of formaldehyde and 0.679 g. of ammonia, according to the equation. Since the analysis showed that 7.45 g. of formaldehyde and 1.16 g. of ammonia had been liberated, it was apparent that 3.87 g. of formaldehyde and 0.49 g. of ammonia had been produced from hexamethylenetetramine which had decomposed without being nitrated. This decomposition was assumed to have occurred according to the following reaction.



According to this reaction, it was necessary for 3.01 g. of hexamethylenetetramine to have been used up in yielding the excess of formaldehyde (3.87 g.) found by analysis.

Thus, of the 10 g. of hexamethylenetetramine used in the experiment, only 5.57 g. and 3.01 g. or a total of 8.58 g. was accounted for.

It should be mentioned here that 3.01 g. of hexamethylenetetramine, upon decomposing according to Reaction 3, should have liberated 1.46 g. of ammonia instead of the 0.49 g. found. This apparent discrepancy is accounted for later.

Since no methylamine could be detected qualitatively in the acid re-

maining after the nitration, an effort was made to discover whether any unchanged hexamethylenetetramine remained behind in the acid. Dobriner<sup>11</sup> has shown that hexamethylenetetramine gives precipitates with mercuric chloride which differ in composition with the ratio of the chloride to the tetramine. Thus the compounds  $2C_6H_{12}N_4 \cdot 3HgCl_2$  and  $C_6H_{12}N_4 \cdot 6HgCl_2$  are formed under certain conditions.

After it had been proved by experiment that trimethylenetrinitramine does not form a precipitate with mercuric chloride, the drowned acid from the nitration experiment was neutralized and the solution allowed to evaporate at low temperature to small volume; it was then treated with a saturated aqueous solution of mercuric chloride. A white flocculent precipitate formed immediately; it was filtered off quickly and washed free from mercuric chloride with alcohol. The amount of the precipitate formed was 10.00 g. An analysis showed that it consisted of 85.35% of mercuric chloride and 14.65% of organic material. This indicated that 1.465 g. of the hexamethylenetetramine used in the experiment had not been acted upon as indicated by either Reaction 2 or 3. By adding the 1.465 g. of hexamethylenetetramine so obtained to the 8.58 g. accounted for above, a total of 10.045 g. is obtained, a close agreement with the 10 g. which was added to the nitrating acid.

This experiment served its purpose in showing that the difficulty of obtaining yields of trimethylenetrinitramine greater than 68% was partly due to hydrolysis which occurred concomitantly with the nitration. It was not considered justifiable, however, to conclude that some hexamethylenetetramine remained unchanged in the acid solution even though this was indicated. Considering the readiness with which the tetramine reacts with acids in general and the large excess of nitric acid used in the experiment, it was almost inconceivable that as much as 14% of the material could remain unaltered. It was thought most likely that in addition to Reactions 2 and 3, another reaction was also occurring, namely, the formation of the compound  $C_6H_{12}N_4 \cdot 2HNO_3$  discussed earlier in the paper. This compound, being readily soluble in water, would remain in the nitrating acid when the latter was drowned to cause the trimethylenetrinitramine to separate. Upon neutralizing the drowned acid the tetramine would be set free and its presence shown upon the addition of mercuric chloride as previously described. That such was the case was proved by carrying out an additional nitration with 100% c. p. acid, in which specially purified hexamethylenetetramine was used. The tetramine was purified by solution in water, precipitation with alcohol, then recrystallization from alcohol and finally solution of the crystals again in alcohol and precipitation with ether. At the end of the nitration the spent acid was diluted just to the point of separation of the trinitramine, in order to precipitate

<sup>11</sup> Dobriner, *Z. anal. Chem.*, **36**, 44 (1897).

also some of the nitrate if it were present. The product was collected on a filter and washed rapidly once with ice water, then several times with alcohol at  $-5^{\circ}$  and finally twice with cold ether. The washing was done in this manner to prevent decomposition or solution of any hexamethylenetetramine nitrate that might be present. It was found that the trinitramine was contaminated with the nitrate, thus indicating that probably in all previous experiments the nitrate had been formed and for this reason a portion of the tetramine had not been converted to the triamine for nitration to trimethylenetrinitramine.

One other point in connection with the nitration in a closed system remained to be explained, namely, the failure to find ammonia in the spent nitrating acid equivalent to the formaldehyde obtained, assuming that the decomposition occurred according to Reaction 3. It was thought that a part of the ammonia probably reacted with the small amount of nitrous acid in the original acid, to give ammonium nitrite which would decompose, even at the low temperature, as follows:  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ . Since no provision was made to collect the nitrogen, it would have escaped without detection.

A second nitration in a closed system and under an atmosphere of carbon dioxide was made, using 1 g. of hexamethylenetetramine and acid similar to that used in the first nitration. The system was connected with a Schiff nitrometer filled with potassium hydroxide to absorb the carbon dioxide. During the addition of the tetramine about 15 cc. of gas was collected. The nitrating mixture continued to evolve the gas slowly. Since no gas but nitrogen could have been liberated and unabsorbed by the potassium hydroxide, the result of the experiment was considered sufficient proof that the loss of ammonia in the first nitration was due to its reaction with nitrous acid and subsequent decomposition according to the reaction just given.

Upon considering the above results as a whole it was thought that a higher yield than had been obtained previously might be obtained if 100% nitric acid were used, thus preventing hydrolysis (Reaction 3) and at the same time promoting nitration of the tetramine nitrate that was evidently formed in almost all of the previous experiments. This concentration of acid had previously given low yields but the temperatures were fairly high, the conditions having been established somewhat on the basis of the procedure given in Herz's patent. Accordingly, a temperature of  $-20^{\circ}$  was chosen for three additional nitrations (Expts. 23, 24 and 25). Ten g. of hexamethylenetetramine, specially purified as described above and 150 g. of nitric acid of concentration 100%, 94 and 80%, respectively, were used. The nitric acid upon analysis showed the following composition: nitric acid, 99.83%; nitrogen tetroxide, 0.12%; water, 0.05%. The time for the addition of the salt was 140 minutes, and the time before

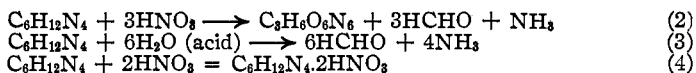


drowning 15 minutes. In the first two experiments 74.4 and 73.9% yields were obtained, respectively. In Expt. 25 only a trace was obtained, as hexamethylenetetramine nitrate separated before drowning the acid; no trinitramine was obtained upon drowning.

Expts. 23 and 24 gave yields about 6% higher than any obtained previously. That acid of lower concentration causes the formation of the nitrate to such an extent as to give practically none of the trinitramine was shown by Expt. 25. In this case the nitrate separated before drowning the acid. Upon decanting and then diluting, about 3 g. of material was obtained. This was not the trinitramine, however, for when washed with water it gradually disappeared. This, of course, indicated that it was hexamethylenetetramine nitrate.

### Discussion

The experiments described above show that upon the addition of hexamethylenetetramine to concd. nitric acid three separate and distinct reactions occur. These are Reactions 2, 3 and 4.



With acid of comparatively low concentration, up to 70%, the process proceeds as indicated by Reaction 3 and little or no nitration is effected. With somewhat higher concentrations, 80–85% nitric acid, Reactions 3 and 4 occur, while at still higher concentrations all three reactions occur at the same time, Reaction 2 predominating at the highest concentrations, 95–100%, when the acid is maintained at a low temperature and other conditions, such as rate of addition of the tetramine, etc., are favorable. With 100% acid at low temperature, Reaction 3 is practically eliminated owing to the absence of water, and the conditions are most favorable for high yields of the trinitramine, in so far as Reactions 2 and 3 are concerned; yields approaching 100% are not obtained, however, because Reaction 4 occurs to a certain extent, the nitrate being fairly stable in the nitric acid at low temperature. The highest yield obtainable appears to be about 75%.

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### Summary

1. In nitrating hexamethylenetetramine to obtain trimethylenetrinitramine, the highest yields were given by concd. nitric acid at low temperatures. Yields higher than 75% could not be obtained owing to the formation of the addition compound  $\text{C}_6\text{H}_{12}\text{N}_4 \cdot 2\text{HNO}_3$ .

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.

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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).