Summary

1.   The differential electrometric method for titration has been adapted to the use of hydrogen electrodes.

2.   The usefulness of the method has been shown by its application to precise acidimetry. Three standards for use in acidimetry: constant boiling hydrochloric acid, potassium acid phthalate and benzoic acid, have been tested and have been shown to be suitable for accurate work (0.01% or better).

New York, N. Y.

THE PHOTOCHEMICAL INTERACTION OF ETHYLENE AND AMMONIA

By Hugh S. Taylor and Harry J. Eméléus[1]

The present work had its origin in some experiments carried out by J. R. Bates at the suggestion of one of us (H. S. T.) in December, 1926, during our studies of photosensitized decompositions by excited mercury.[2] In this work it was found that, in the decomposition of ammonia, both photochemically and by excited mercury, the non-condensable gas first received in a flowing system was mainly hydrogen. This suggested a primary decomposition of ammonia into NH_2 and H, and experiments were undertaken to determine whether evidence for this could be obtained from reactions initiated by such atomic hydrogen. This was readily forthcoming, since we showed that the photochemical decomposition of ammonia in presence of hydrogen and carbon monoxide led to very much larger yields of formaldehyde than were obtained under the same arc conditions in the absence of ammonia. This latter fact was also proof that we were not producing the formaldehyde by reason of the presence of excited mercury in the system. The reaction was sufficiently rapid that a solid residue was quickly laid down on the vessel walls; the solid was assumed to be hexamethylenetetramine. We have not yet examined the reaction further, and therefore confine ourselves to recording at this time the free solubility of the solid product in water.

In the following year Hill and Vernon,[3] at Princeton, also showed that the illumination of ammonia in the far ultraviolet and at low partial pressures, in quartz vessels, in contact with tungstic oxide gave an immediate reduction to the blue oxide. This again pointed to atomic hydrogen, but not so directly, since hydrazine might have been the product to

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[1] Commonwealth Fund Fellow.

[2] Bates and Taylor, This Journal, 49, 2438 (1927).

[3] Unpublished experiments.

which such reduction was to be attributed. Further work in this very promising field had to be postponed pending the erection of a new laboratory in which facilities were available for the development of light sources of high intensity in the region absorbed by ammonia. These were obtained last year, and the present program was then initiated.

During the latter part of 1929 an apparatus was assembled to study the sensitization of the hydrogen–ethylene reaction by atomic hydrogen produced in the photo-decomposition of ammonia. Before the release of the high tension spark sources from other work,[4] a communication by Farkas, Haber and Harteck[5] on the photosensitization of the oxidation of hydrogen and carbon monoxide by means of ammonia indicated that the field of ammonia sensitization was being pursued elsewhere. We have, therefore, utilized, in the present work, the available mercury light sources of the laboratory in continuation of the program initiated as described above.

Our choice of the ethylene–hydrogen reaction for study was dictated by several reasons. In the presence of excited mercury the reaction has been very fully investigated,[6] and the various possible reactions identified. The reactions are fast, and their progress can be followed manometrically. With oxygen as one of the reactants in the system, there is always the possibility that the primary interaction of ammonia with oxygen might influence the results. The deposition of solid products in the hydrogen–carbon monoxide reaction ascertained in the first experiments was the principal factor in our choice of the hydrogen–ethylene reaction. We anticipated straightforward gas reactions in the case of hydrogen and ethylene but our experiments have shown that the deposition of liquid products is the principal reaction, and these inhibit, in part, the reactions occurring.

We shall present first the nature of the experimental procedure and the experimental results. A general discussion of the data obtained will then be given.

Experimental Details

Ethylene was prepared by washing the gas from a cylinder with sulfuric acid and condensing in liquid air, dissolved non-condensable gases being then removed by melting in vacuum, freezing, and re-evacuating. Approximately one-quarter of the condensate was pumped off at its melting point, and the bulk of the liquid was then distilled at −100° in vacuum directly into the storage globe. Ammonia was prepared similarly, the gas from a cylinder being frozen in liquid air, freed from dissolved gases and a middle fraction collected by distilling from a bath at −100°. Commercial electrolytic hydrogen was purified by passing over heated platinized asbestos, and drying with phosphorus pentoxide. Gas mixtures were prepared by admitting the gases in turn into the previously evacuated reaction vessel up to the required pressure, as indicated by a mercury manometer.

4 Kistiakowsky, THIS JOURNAL, **52,** 1868 (1930).

5 Farkas, Haber and Harteck, *Naturwissenschaften,* **12,** 267 (1930).

6 Taylor and Hill, THIS JOURNAL, **51,** 2922 (1929).

The mercury arc was of the vertical type, uncooled and normally operated at about 2.5 amp. from the 110-volt d. c. circuit. The region absorbed by ammonia lies almost at the limit of transmission of quartz, and the available radiation of this wave length was found to fluctuate from one experiment to another. For this reason the results of different experiments cannot, in general, be compared with one another. In some cases, however, as, for example, in the comparison of the decomposition of ammonia with and without ethylene, comparable conditions were maintained for two sets of observations.

Two reaction vessels were employed. A cylindrical bulb of quartz (Vessel A) 16 cm. long by 2.5 cm. diameter was used when temperature conditions were of secondary importance. It was illuminated from one side by the vertical arc. Reaction vessel B was an annulus of quartz, of 7.5 cm. external diameter, 4.5 cm. internal diameter and 10.5 cm. long, which was immersed in a constant-temperature water-bath and illuminated by a vertical arc placed co-axially within the annulus. The reaction vessels were cleaned between successive experiments by evacuating, filling with oxygen, and heating to a red heat. The film of oil deposited during the reaction was completely removed in this way.

Experimental Results

General Course of the Reaction.—A mixture of ethylene and ammonia when illuminated in quartz reaction bulb A, with the mercury arc placed at a distance of 1 cm., showed a steady decrease of pressure, the reaction being followed by interrupting the illumination, and measuring the pressure with the bulb immersed in a bath at 20° and in liquid air. Such a series of observations is recorded below.

TABLE I

PRESSURE VARIATION ON ILLUMINATION OF 10.05 CM. OF ETHYLENE AND 2.23 CM. OF AMMONIA

Time of illumination	Total pressure, cm.	Pressure of non-condensable gas (corrected to 20°), cm.
0 Minutes	12.28	0.00
25	9.32	.16
50	7.45	.00
80	5.95	.39
105	5.17	.58
170	4.45	.80
316	4.38	1.54
496	4.50	1.71
760	4.72	2.15
27 Hours	5.13	2.77
32[a]	5.62	3.25
34.5	5.87	3.89
62.5	6.07	4.05

[a] At this point the position of the arc was shifted to the opposite side of the reaction vessel, and its distance altered from 1 cm. to 0.5 cm.

As the reaction progressed a light brown oil was deposited, which was found to retard the reaction, due, probably, to a reduction of the effective light intensity. This is shown by the following measurements. An ethylene–ammonia mixture ($p_{C_2H_4}$, 9.97 cm.; p_{NH_3}, 10.45 cm.) was illumi-

nated for 160 minutes, and gave a pressure reduction of 2.84 cm. After evacuating the reaction bulb (the oil not being appreciably volatile), a fresh gas mixture was admitted ($p_{C_2H_4}$, 9.80 cm.; p_{NH_3}, 10.21 cm.). Continuing the illumination under the same conditions, the decrease in pressure in fifty minutes was only 0.24 cm. Moreover, the reaction rate at the beginning of the second experiment was approximately the same as that at the point where the first was interrupted.

On illuminating ammonia in the reaction vessel in which an ethylene–ammonia mixture had reacted with a pressure reduction of 1.86 cm., the ammonia decomposition resulted in a pressure increase of 0.07 cm. in ten minutes, whereas the average value for ammonia under the same conditions in a clean vessel was 0.24 cm. in ten minutes, showing that the oil also retarded the decomposition of ammonia.

Illumination of Ethylene Alone.—On illuminating ethylene alone with the mercury arc in vessel A illuminated at 1 cm. distance there was a reaction, the rate of decrease of pressure being approximately 20–30% of that observed with ammonia present. This is shown by the following measurements.

<div align="center">TABLE II</div>
<div align="center">COMPARISON OF PHOTOCHEMICAL ACTION WITH AND WITHOUT AMMONIA</div>

$p_{C_2H_4}$, cm.	p_{NH_3}, cm.	Time of illumination, min.	Pressure decrease, cm.
30.53	..	45	1.97
33.22	6.66	45	6.17
17.87	..	30	0.63
18.01	3.68	30	4.14

With a hot arc this reaction cannot be due to a mercury sensitized reaction, and probably represents a direct polymerization following absorption by the ethylene itself. Using reaction vessel B the polymerization of ethylene without ammonia becomes inappreciable. Thus, with this vessel and with $p_{C_2H_4}$ = 14.64 cm., the pressure decrease on illuminating for 140 minutes was 0.12 cm.; with $p_{C_2H_4}$ = 32.57 cm., the pressure decrease on illuminating for ninety minutes was 0.10 cm.

In experiments with reaction vessel A the reaction of ethylene alone was neglected, these runs being made mainly in the investigation of the products of the reaction. Reaction vessel B was used in studying the kinetics of the reaction, and in that case the reaction of ethylene alone was some 5% of that in the presence of ammonia.

Formation of Saturated and Unsaturated Hydrocarbons in the Reaction.—To determine whether saturated hydrocarbons were formed in the course of the reaction, an ethylene–ammonia mixture was illuminated in vessel A and the non-condensable gas pumped off with the bulb immersed in liquid air. The residue was then distilled in vacuum into a bulb containing gas-free 10% sulfuric acid to absorb ammonia and amines. The

moist residue was returned to the reaction vessel and the pressure re-measured. The percentage of unsaturated hydrocarbon in this residue was then determined by absorption with fuming sulfuric acid. Where the quantity of gas was sufficient, a sample was pumped off and oxidized over copper oxide heated to a red heat, the increase in pressure on oxidation and the decrease on treating the residue with potash giving the number of carbon atoms in the molecule. Two experiments were also made in which hydrogen was introduced to determine whether this caused an increase in the amount of saturated hydrocarbon formed. These results are recorded below. Those in which hydrogen was present are discussed later.

TABLE III

FORMATION OF SATURATED AND UNSATURATED HYDROCARBONS

	$p_{C_2H_4}$	p_{NH_3}	p_{H_2}	Δp in reaction, cm.	Time, hours	% of residual gas absorbed by fuming H_2SO_4	Carbon value
1	38.80	6.17	...	10.88	10.5	94	...
2	32.67	5.47	...	12.11	15	93	2.0
3	24.72	7.00	11.89	11.12	16	89	...
4	30.33	8.33	13.73	12.01	15	93	2.1
5	33.68	5.92	...	12.18	5.25	92	...

These results show that in the course of the reaction a small amount of gas not absorbed by fuming sulfuric acid was formed, which must be saturated hydrocarbon. It is very probable that this residue consists of ethane. The approximation of the carbon value for the total residue to the value C_2 shows that the residue contained no appreciable amounts of the higher homologs of ethylene—it must have consisted in the main of unchanged ethylene.

Influence of Hydrogen on the Reaction.—The mercury sensitized re-action between ethylene and hydrogen was proved not to occur under the conditions of illumination used by radiating an ethylene–hydrogen mixture (p_{H_2}, 15.66 cm.; $p_{C_2H_4}$, 5.43 cm.) in the reaction vessel B. Mixtures of ethylene, hydrogen and ammonia were next illuminated in the simple cylindrical bulb to determine if, under these conditions, the hydrogen re-acted, the hydrogen pressure being measured before and after each run by immersing the reaction bulb in liquid air.

TABLE IV

INFLUENCE OF HYDROGEN ON THE REACTION

	p_{H_2}, cm.	p_{NH_3}, cm.	$p_{C_2H_4}$, cm.	Time, min.	Total Δp, cm.	Initial p_{H_2} at $-180°$, cm.	Final p_{H_2} at $-180°$ cm.
1	10.06	2.34	10.05	72	−4.09	3.29	3.41
2	10.06	10.03	10.08	38	−2.43	3.36	3.34
3	20.12	9.90	10.09	97	−8.53	6.98	6.97

From the last two columns it is evident that the amount of hydrogen used in the reaction is negligible. Further support for this conclusion is

obtained from the analyses recorded above, where it was shown that, in presence of hydrogen, there was no difference in the amount of saturated hydrocarbon formed.

Reaction of Ammonia.—In the presence of ethylene, ammonia might be expected either to undergo its normal decomposition into nitrogen and hydrogen, or to react with the hydrocarbon, giving amines as the main product. To determine the extent to which the normal decomposition occurred, ammonia was illuminated in the quartz reaction bulb A with the mercury arc for a definite time and the amount of non-condensable gas formed determined by immersing the bulb in liquid air at the end of the run. An ethylene–ammonia mixture with the same pressure of ammonia was then illuminated for the same time·under identical conditions, and the non-condensable gas again determined.

TABLE V

AMMONIA DECOMPOSITION WITH AND WITHOUT ETHYLENE

	p_{NH_3}, cm.	Δp, cm.	Time of illumina- tion, min.	$p_{l.a.}$, cm.	p_{NH_3}, cm.	$p\,C_2H_4$, cm.	Δp, cm.	Time, min.	$p_{l.a.}$, cm.
1	5.17	+1.42	45	1.02	5.03	14.75	−5.38	50	0.05
2	4.95	1.30	40	0.76	5.11	15.26	..	40	.03
3	10.00	0.95	63	.65	10.03	15.00	−4.29	63	− .01

The readings under $p_{l.a.}$ refer to the pressure of non-condensable gas at liquid air temperatures. Other pressure measurements were made at 20°. These readings show that in the presence of ethylene the simple decomposition of ammonia was reduced to less than 10% of its normal value.

The second possibility, namely, the formation of a simple compound, should be indicated by a definite relation between the amount of ammonia which would normally have decomposed under the conditions of illumination used, and the amount of ethylene used. The total decrease in pressure in the reaction has been used as a measure of the latter quantity; actually this measures the minimum value of this quantity, for the true pressure decrease will be reduced by the formation of other volatile products (such as amines, and saturated and unsaturated hydrocarbons).

A series of observations of this type was conducted in reaction vessel B maintained at·room temperature. The ammonia decomposition rate was first determined over a period of forty to eighty minutes, the residue being then pumped out and an ammonia–ethylene mixture introduced, the arc conditions remaining unchanged. The decrease in pressure over the first ten to twenty minutes was determined, this short period of illumination minimizing the error due to the accumulation of oil.

The average value of r is 5.0. This measures the ratio of the pressure decrease in presence of ethylene to the pressure increase due to the simple ammonia decomposition. That is, for every one molecule of ammonia which would have decomposed, at least five molecules of ethylene disap-

TABLE VI

AMMONIA DECOMPOSITION WITH AND WITHOUT ETHYLENE

	p_{NH_3}	Δp in 10 minutes, cm.	p_{NH_3}	$p_{C_2H_4}$	Δp in 10 minutes, cm.	r
1	4.77	0.095	4.86	15.15	−0.42	4.4
2	5.03	.098	5.06	15.15	− .46	4.7
3	5.08	.085	5.00	15.15	− .44	5.2
4	5.05	.052	5.00	15.13	− .28	5.4
5	5.05	.049	5.11	15.07	− .235	4.8
6	4.95	.045	5.07	15.07	− .245	5.4

pear. The high value of this ratio is strongly against the formation of a simple compound, such as a volatile amine. Even for a tertiary amine the ratio would be only 3, and it appears very probable that the ethylene has undergone a polymerization, resulting in the deposition of the non-volatile oil.

As a further check on the disappearance of ammonia in the reaction, four runs were made in which the residual ammonia (+ amines) was determined, after varying times of illumination, by admitting 1–2 cc. of 30% sulfuric acid directly into the reaction vessel from a side tube, the observed decrease in pressure being corrected for the vapor pressure of the acid.

TABLE VII

RESIDUAL AMMONIA (OR AMINES) AFTER ILLUMINATION

	p_{NH_3}	$p_{C_2H_4}$	Time of illumination, min.	Δp, cm.	Gas absorbed as % of original ammonia
1	5.50	19.59	30	− 3.71	96
2	5.25	19.93	60	− 5.30	92
3	5.75	19.95	120	− 9.20	78
4	5.62	19.76	210	−11.68	62

If a part of the ethylene had formed a volatile amine, then, for every ammonia molecule decomposed, one molecule of amine should have been formed, and the gas absorbed by sulfuric acid should have remained constant throughout a run. The above table shows that such is not the case; that is, volatile amine formation must have occurred to a very much smaller extent, if at all.

Finally, an attempt was made to determine whether the amount of ammonia decomposed in the presence of ethylene was the same as that which would be observed on illuminating ammonia alone under the same conditions. Ammonia was first illuminated, the pressure change in a definite time being measured. An ethylene–ammonia mixture was then illuminated under the same conditions, and for the same time, and the residual ammonia determined by introducing 10% sulfuric acid directly into the reaction bulb. The following values were obtained.

These results show that within the probable error of the experiments the ammonia decomposition proceeded normally in presence of ethylene,

TABLE VIII

AMMONIA DECOMPOSITION WITH AND WITHOUT ETHYLENE

	Pressure of ammonia decomposed measured by pressure change, ethylene absent, cm.	Measured by absorption ethylene present, cm.
Expts. Ia and b	0.79	0.93
Expts. IIa and b	1.00	.80
Expts. IIIa and b	1.08	.97

the products of the reaction alone being different. The non-condensable gas formed in the reaction was pumped off in two experiments, and analyzed for hydrogen and nitrogen by burning over copper oxide. With $p_{C_2H_4}$ = 15.01 cm., p_{NH_3} = 10.05 cm., and with a pressure decrease of 10.36 cm. in the reaction, the pressure of non-condensable gas formed, measured at liquid-air temperatures, was 0.33 cm., and 84% was found to be absorbed by heated copper oxide. In a repetition of this run the value 83% was obtained.

The oil deposited during the reaction was not available in sufficient quantity for further examination. It was insoluble in water and acids, and soluble with difficulty in ether. A similar oil was formed in the polymerization of ethylene sensitized by excited mercury.[6] In the present case, however, it is impossible to account for the nitrogen from the decomposed ammonia except by supposing it to be present in the oil in the form of compounds of low volatility. Vapor pressure measurements made on the residue in the reaction bulb after pumping off all gas volatile at −100 to −90° were as follows.

TABLE IX

VAPOR PRESSURES OF OILY RESIDUE

Temperature, °C.	−76	−58	−44	−30
V. p., cm.	0.05	0.10	0.19	0.34

It is obvious that such measurements have minor value since the residue is undoubtedly complex. We believe the evidence presented indicates polymerization of the ethylene with the participation of the NH_2 radical at some stage of the total process later than the first stage, since this would involve volatile amine production.

Reaction Kinetics

Influence of Ethylene Concentration on the Reaction Rate.—These experiments were made in vessel B at room temperatures. A measured pressure of ammonia was admitted to the bulb, and then a small pressure of ethylene, the decrease in pressure on illumination for ten minutes being determined. After introducing a further quantity of ethylene the rate was re-determined, and so on for a series of ethylene pressures. The retardation of the reaction due to the deposition of oil was determined by

working with fixed amounts of ethylene and ammonia, and measuring the pressure at ten-minute intervals (Expt. 1). By comparing this set of readings with those in which the ethylene concentration was varied, it was possible to determine if the latter had any influence on the rate.

TABLE X

INFLUENCE OF ETHYLENE CONCENTRATION ON REACTION RATE

Expt. 1. $p_{C_2H_4}$, 32.47 cm. p_{NH_3}, 5.17 cm.

Time, min.	10	20	30	40	·50	60
Δp in 10 min., cm.	−0.26	−0.30	−0.24	−0.23	−0.22	−0.20

Expt. 2. p_{NH_3}, 4.98 cm.

$p_{C_2H_4}$, cm.	4.7	9.35	14.4	19.1	28.3
Δp in 10 min., cm.	−0.44	−0.42	−0.40	−0.38	−0.38

Expt. 3. p_{NH_3}, 10.03 cm.

$p_{C_2H_4}$, cm.	1.0	4.4	9.6	22.3
Δp in 10 min., cm.	−0.27	−0.24	−0.29	−0.26

Expt. 4. p_{NH_3}, 18.8 cm.

$p_{C_2H_4}$, cm.	0.9	2.3	5.25	13.9
Δp in 10 min., cm.	−0.12	−0.12	−0.10	−0.14

These results show that over a wide concentration range the rate of reaction is independent of the ethylene pressure.

Influence of Ammonia Concentration on the Reaction Rate.—The same method was used in studying the influence of ammonia concentration on the reaction rate, a fixed pressure of ethylene being used while the ammonia concentration was varied. As the reaction progressed the ethylene concentration decreased, but it has already been shown that this does not influence the rate. Similarly, in the previous set of observations, the ammonia concentration must have decreased; this effect has been neglected, a course which is justified by the results given below.

TABLE XI

INFLUENCE OF AMMONIA CONCENTRATION ON REACTION RATE

Expt. 1. $p_{C_2H_4}$, 20.99 cm.

p_{NH_3}, cm.	0.9	3.1	9.0	12.0
Δp in 10 min., cm.	−0.13	−0.22	−0.22	−0.18

Expt. 2. $p_{C_2H_4}$, 10.03 cm.

p_{NH_3}, cm.	0.3	0.8	1.8	4.4	9.6
Δp in 10 min., cm.	−0.08	−0.15	−0.21	−0.19	−0.20

Expt. 3.   In this experiment the ammonia was introduced as a mixture with hydrogen containing 16% of ammonia. $p_{C_2H_4}$, 10.03 cm.

p_{NH_3}, cm.	0.04	0.12	0.22	0.38	1.14
Δp in 10 min., cm.	−0.05	−0.08	−0.11	−0.13	−0.18

These results show that above a certain pressure the rate of reaction is independent of the ammonia pressure. This pressure is approximately

equal to 1.5 cm., and may be interpreted as being the pressure at which the active light is completely absorbed. Below this point the reaction rate increases with increasing ammonia concentration, but the accuracy of the measurements does not justify any attempt to formulate a relation between the two.

Temperature Coefficient of the Reaction.—The approximate temperature coefficient of the reaction was determined by working with reaction vessel B placed in a water-bath which could either be maintained at 15° or heated at 98°. The radiation emitted by the arc was found to be very sensitive to temperature for the wave length region absorbed by ammonia, and the decomposition of ammonia itself, for which the temperature coefficient is known, was used as a method of calibration. The ammonia decomposition was found to have an apparent temperature coefficient of 3.1 for a temperature increase of 83°. From Kuhn's value of 1.05 per 10°, the factor should be 1.4. Taking this discrepancy as due to a change in the condition of the arc, the observed values for the temperature coefficient (of the ethylene–ammonia reaction) were divided by the factor 3.1/1.4 = 2.2, to give the true values.

Ammonia Decomposition.—In a series of runs in which the pressure of ammonia was varied from 3 cm. to 18 cm., the following values were obtained for the ratio of the decomposition rate at 98° to that at 15°: 3.4, 3.7, 3.9, 2.4, 3.9, 2.9, 2.8, 2.4, 2.7; average, 3.1.

Ethylene–Ammonia Reaction.—The following measurements were made with ethylene–ammonia mixtures, the reaction vessel being cleaned and the arc reset between the measurements at the two temperatures.

	15°				98°			
p_{NH_3}, cm.	$p_{C_2H_4}$, cm.	Δp, cm.	Time, min.	p_{HN_3}, cm.	$p_{C_3H_4}$, cm.	Δp, cm.	Time, min.	r
3.03	15.13	−0.94	30	3.09	14.94	−2.48	30	2.64
5.08	15.24	−1.29	40	5.05	15.40	−2.03	25	2.52
5.41	15.05	−1.67	60	5.40	14.96	−1.85	20	3.33
5.02	15.10	−1.86	60	5.05	15.05	−1.90	20	3.06

The value of r in the last column is the ratio of the pressure decrease at 98° to that at 15° calculated for equal times of reaction.

The average value of r is 2.9, *i. e.*, dividing by the factor 2.2, the temperature coefficient for 83° is 1.32 or 1.04 per 10°. Taking into account the low degree of accuracy of the determinations, this value does not differ sensibly from that for the photo-decomposition of ammonia.

Discussion of Results

A survey of the data obtained in the preceding sections justifies the general conclusion that the photochemical decomposition of ammonia induces the low-temperature polymerization of ethylene. We ascribe this induced polymerization to the liberation, in the reaction system, of atomic

hydrogen formed in the decomposition of ammonia. At some stage in the process, however, the nitrogen fragment of the dissociation enters the reaction and is removed not as a volatile amine, but as a liquid, non-volatile, nitrogen carbon compound of undetermined composition.

The polymerization of ethylene with the aid of atomic hydrogen is a familiar process by reason of earlier work on excited mercury. In the latter case, however, polymerization is always accompanied by hydrogenation, which, with hydrogen-rich mixtures, may even be practically the exclusive reaction.[6] This result is in striking contrast to the present work with ammonia as the source of atomic hydrogen. Here we find the hydrogenation occurring to be of the order of 20% of the ethylene polymerized. It is evidently necessary, therefore, to account for such a divergence of behavior. The reaction with ammonia is as much a process of polymerization as that found by Taylor and Jones,[7] in which ethyl radicals liberated from decomposing metal ethyls in mixtures of hydrogen and ethylene at 250° produced mainly ethylene polymers with only small amounts of saturated hydrocarbons.

Experimentally, the outstanding divergence between the processes with ammonia and with mercury is probably associated with the concentration of atomic hydrogen produced. In the case of mercury, as has frequently been pointed out, the reaction volume is mainly confined to a very thin element of volume adjacent to the vessel surfaces receiving illumination by resonance radiation, owing to the extremely high absorption coefficient of mercury atoms for this light. Comparatively, in the case of ammonia, the concentration of atomic hydrogen produced is very much less.

That saturated hydrocarbon formation is small with ammonia in hydrogen–ethylene mixtures at room temperatures and is subordinate with metal alkyls even at 250° suggests definitely that a reaction $C_2H_5 + H_2 = C_2H_6 + H$,[8] postulated in earlier communications[2,6] on this subject to account for ethane formation, must in reality be a reaction of low collision efficiency. This conclusion is in agreement with a wide variety of experience accumulated in the past year,[4,9,10,11] concerning the reactivity of the atoms and radicals, O, Cl, F, CHO with hydrogen molecules. The formation of hydrogen peroxide to the exclusion of water at ordinary temperatures from atomic hydrogen and oxygen molecules[2] also points to the inefficiency of collisions in the process, $OH + H_2 = H_2O + H$. We are led, therefore, to reject the reaction $C_2H_5 + H_2 = C_2H_6 + H$ as the process producing saturated hydrocarbon at ordinary temperatures. At 250° and higher

[7] Taylor and Jones, This Journal, **52**, 1111 (1930).

[8] The production of ethyl from hydrogen atoms and ethylene is an association reaction $H + C_2H_4 = C_2H_5$ to be achieved by means of a three-body process.

[9] Frankenburger, Z. Elektrochem., **36**, 757 (1930).

[10] Farkas, Haber and Harteck, ibid., **36**, 714 (1930).

[11] Franck and Rabinowitsch, ibid., **36**, 794 (1930).

such a process may have a measurable efficiency. Even there, however, it must play a subordinate role to processes of polymerization involved in collisions between C_2H_5, C_4H_9, etc., and unsaturated molecules, $C_2H_5 + C_2H_4 = C_4H_9$. Such association reactions must be three-body processes to produce stabilized products. They are, however, more frequent than another three-body process producing amine $C_2H_5 + NH_2 = C_2H_5NH_2$, owing to the high concentration of C_2H_4 compared with that of NH_2. This accounts for the absence of the lower volatile amines in the gas phase, a circumstance which is aided by the fact that such amines are themselves photochemically decomposed. The presence of nitrogen compounds in the liquid deposit indicates, however, that processes such as $C_nH_{2n+1} + NH_2 \longrightarrow C_nH_{2n+1}NH_2$ occur at later stages in the polymerization processes.

There remains the problem as to the mechanism of saturated hydrocarbon formation in excited mercury systems at ordinary temperatures. If we exclude the reaction $C_2H_5 + H_2 = C_2H_6 + H$ for reasons already set forth, we are left with the following possibilities already discussed in an earlier communication,[6] (a) $C_2H_4 + H_2 + H = C_2H_6 + H$ and (b) $C_2H_5 + C_2H_5 = C_2H_6 + C_2H_4$, together with one additional possibility not hitherto noted, (c) $C_2H_5 + HgH = C_2H_6 + Hg$. Concerning these we can make the following additional observations in the light of the new results. A reaction of type (a) should occur equally efficiently with a hydrogen atom from an ammonia molecule as with one from excited mercury and hence, in view of our experimental data with ammonia indicating low conversion to saturates, is to be considered of minor importance. Reactions of the type (b) and (c) are only to be expected in regions of high concentration of atoms or the resultant radicals and thus may be anticipated in the mercury systems and not in the ammonia system. It is to be noted that reaction (b) is a strongly exothermic process involving the evolution of some 70 kg. cal.,[12] with probably a very low activation energy. That both reactions (b) and (c) are bimolecular and are not association reactions gives them a higher degree of probability than similar reactions of two radicals involving three-body processes, e. g., $C_2H_5 + C_2H_5 + X = C_4H_{10} + X$.

Summary

The photochemical decomposition of ammonia in the presence of ethylene or ethylene–hydrogen mixtures induces a polymerization of the ethylene, even at room temperatures, to form a liquid product.

The formation of saturated hydrocarbons in the reaction system with varied ratios of hydrogen to ethylene is subordinate to the polymerization process.

The presence of ethylene reduces the formation of nitrogen and hydrogen from photo-decomposition of the ammonia. The nitrogen content of the

[12] Mecke. *Z. Elektrochem.*, **36**, 595 (1930).

ammonia decomposed must be present mainly in the oil produced, in the form of compounds of low volatility.

The velocity of reaction is independent of the ethylene pressure over a wide concentration range and of the ammonia pressure when light absorption is complete.

The temperature coefficient of the total process is determined by that of the photo-decomposition of ammonia.

The experimental results lead to definite conclusions with regard to the efficiency of various possible methods of producing saturated hydrocarbons from ethylene and atomic hydrogen.

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AN EFFECT OF THE BREADTH OF JUNCTION ON THE ELECTROMOTIVE FORCE OF A SIMPLE CONCENTRATION CELL[1]

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It is generally assumed that the electromotive force of a simple concentration cell, such as M, MX(m_1), MX(m_2), M, is independent of the method of making the junction between the two solutions, and that this fact has been demonstrated both theoretically and experimentally. The same theoretical argument may be extended to any cell involving a liquid junction to show that the electromotive force is independent of the thickness of the boundary layer provided that any element of the solution may be duplicated by taking x parts of the solution surrounding one electrode and $(1 - x)$ parts of that surrounding the other electrode.[2] Such a boundary is known as a "mixture boundary" and is obtained in practice when the boundary is made without diffusion. A simple concentration cell must always give a "mixture boundary" regardless of diffusion.

The electromotive force of a cell with electrodes reversible to the k'th ion, when the temperature and pressure are constant throughout the cell, is given by

$$E = \sum_{i=1}^{n} \int_{B}^{A} t_i dE_{ik} = \frac{RT}{F} \sum_{i=1}^{n} \int_{B}^{A} t_i \, d \ln \frac{(m_i \gamma_i)^{1/z_i}}{(m_k \gamma_k)^{1/z_k}}$$

where R is the gas constant, T the absolute temperature, F the faraday, t_i is the transference number of the i'th type of ion, z_i is its valence (taken negative for a negative ion), m_i its molality, and γ_i its activity coefficient.[3]

[1] Presented before the Physical and Inorganic Chemistry Section at the Cincinnati Meeting of the American Chemical Society, September 10, 1930.

[2] P. Henderson, Z. physik. Chem., 59, 118 (1907); 63, 325 (1908).

[3] P. B. Taylor, J. Phys. Chem., 31, 1478 (1927).