[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Temperature Coefficient of the Photosensitized Hydrogen–Oxygen Reaction

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The mechanism of the hydrogen–oxygen reaction at high temperatures has been the subject of considerable discussion recently. All of the schemes postulated for the reaction involve a chain, with either excited molecules or free atoms and radicals as propagating agents. One of the general characteristics of a chain reaction is that there exists a temperature region in which its reaction velocity does not obey the Arrhenius equation $d \ln k/dT = E/RT^2$, but increases more rapidly with temperature than this law demands. Such a reaction is said to possess an anti-Arrhenius temperature coefficient. This behavior arises from the fact that there will be superposed on the ordinary temperature effect, which causes an increase in the number of reactions initiated, an additional temperature effect due to increase in the length of each chain started. As a result of these two influences, the change of reaction velocity with temperature cannot be expressed by a simple law.

The temperature coefficient of the direct photochemical hydrogen–oxygen reaction has been measured by Andrejeff[1] and by Coehn and Grote.[2] These investigators found that the value of k_{t+10}/k_t was only 1.04–1.06 in the range 130–240°. Consequently, increase in temperature did not result in marked increase in chain length in this temperature range. Kistiakowsky[3] showed for the same reaction that, whereas the temperature coefficient was 1.05 at room temperatures, it increased to 1.25 at temperatures above 500°. Kistiakowsky concluded that over a considerable temperature range only short chains existed, but that above 500°, quite long chains were propagated in the illuminated gas mixture.

More recently Farkas, Haber and Harteck[4,5] have determined the chain lengths in hydrogen–oxygen mixtures sensitized to light by ammonia. Their work indicated that water formation proceeded by a chain, the length of which increased exponentially with temperature, as expressed by the empirical equation $l_t = 3\, e^{0.023(t-200)}$, where l_t is the chain length at the temperature t°C.[5] This gives at about 400° a chain of about 350 molecules of water for each hydrogen atom produced by light from the ammonia. Furthermore, explosions occurred at temperatures about 420° and oxygen–hydrogen pressures above 300 mm. These results would

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[1] Andrejeff, *J. Russ. Phys.-Chem. Soc.*, **43**, 1345 (1911).

[2] Coehn and Grote, Nernst-Festschrift, 1912.

[3] Kistiakowsky, *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

[4] Farkas, Haber and Harteck, *Naturwissenschaften*, **18**, 266 (1930); *Z. Elektrochem.*, **36**, 711 (1930).

[5] Haber, *Naturwissenschaften*, **18**, 917 (1930).

indicate that the chains were lengthening rapidly as the temperature increased, becoming very long at comparatively low temperatures. To explain their findings, these authors used the Bonhoeffer–Haber mechanism of water formation,[4,5,6,7] which postulates chain propagation by means of hydrogen atoms and hydroxyl radicals. To explain the explosions, it was suggested in addition that chain branching could occur through a reaction producing two hydroxyl radicals.

Now, the results obtained in ammonia–hydrogen–oxygen mixtures are at variance with those of the direct photochemical reaction as measured by Kistiakowsky. The initial difference between the two reactions would seem to lie in the fact that following light absorption, hydrogen atoms are produced in the former whereas oxygen atoms are formed in the latter. The oxygen atoms must, however, react with the hydrogen by the step[8]

$$O + H_2 = OH + H \qquad (1)$$

Although reaction step (1) has a small activation energy, it should be completely efficient at about 400°. Therefore, if the Haber mechanism be correct, both the OH radical and the H atom could initiate a chain. Consequently, it is to be expected that chain lengths in both the direct photochemical and the ammonia sensitized reaction should be about the same at comparable temperatures. This does not appear to be the case.

Hydrogen atoms can be produced at high temperatures from the action of excited mercury on molecular hydrogen. At ordinary temperatures, Marshall[9] has determined the chain length in the mercury sensitized hydrogen–oxygen reaction, finding an average value of 2.5 molecules per quantum. He also determined the temperature coefficient of the reaction to be 1.04 over a limited temperature range. In view of the discrepancy of the direct photochemical and the ammonia sensitized hydrogen–oxygen reaction, and because of the suitable character of the mercury sensitized reaction, a comparison of the temperature coefficients of the mercury sensitized and the ammonia sensitized reactions is of importance. The anti-Arrhenius behavior of the temperature coefficients should indicate the temperature at which long chains are set up in the reaction mixtures.

The Mercury Sensitized Reaction.—The experiments on the mercury sensitized hydrogen–oxygen reaction were carried out in a circulatory system, in order that the gases could be kept saturated with the mercury contained in a glass spiral saturator. The reaction vessel proper was of quartz, 10 cm. long, 1.8 cm. diameter, and 0.5 mm. wall thickness. It was kept at the desired temperatures by an electric furnace. The source of illumination was a water cooled Cooper–Hewitt mercury arc.

[6] Bonhoeffer and Haber, *Z. physik. Chem.*, **137A**, 363 (1928).

[7] Haber, *Z. angew. Chem.*, **42**, 475 (1929).

[8] Kistiakowsky, THIS JOURNAL, **52**, 1868 (1930).

[9] Marshall, *J. Phys. Chem.*, **30**, 34 (1926); **30**, 1078 (1926); THIS JOURNAL, **54**, 4460 (1932).

Starting in every case with a 2:1 $H_2:O_2$ mixture at 600 mm. total pressure, reaction rates were measured at various temperatures from 280 to 535°, and with mercury pressures of 0.0004, 0.0035, and 0.020 mm. Each individual reaction showed an induction period of one or two minutes, but thereafter progressed at a constant speed, measured by the slope of the straight line portion of the time–dp curves. In order to check the temperature coefficient from time to time, the light intensity of one series

TABLE I

DEPENDENCE OF RATE ON TEMPERATURE

Initial pressure 600 mm. P_{Hg}, 0.0004 mm. Ratio $H_2:O_2$, 2:1

No.	Temp.	dp/dt mm./10 min.	I/I_0	dx/dt
D1	356	3.0	0.166	18.1
D2	451	5.0	.166	30.1
D3	506	7.5	.166	45.2
D4	534	69.5	.166	418.8
H1	289	5.4	.562	9.0
H2	349	9.0	.562	16.0
H3	451	20.5	.562	36.5
H4	506	31.0	.562	55.1
H5	534	108.0	.562	191.9
I1	290	15.0	1.00	15.0
I2	348	17.5	1.00	17.5
I3	405	26.5	1.00	26.5
I4	454	33.5	1.00	33.5
I5	505	47.5	1.00	47.5
I6	534	95.0	1.00	95.0
			P_{Hg}, 0.0035 mm.	
B1	270	8.2	0.860	9.5
B2	404	22.2	.860	25.7
B3	454	27.7	.860	32.2
B4	508	33.5	.860	39.0
A1	271	8.2	.803	10.2
A2	361	16.2	.803	20.2
A3	377	18.3	.803	22.8
A4	403	19.5	.803	24.3
A5	432	21.0	.803	26.2
C1	316	8.5	.595	14.3
C2	345	10.1	.595	17.0
C3	406	15.0	.595	25.2
C4	452	19.0	.595	31.9
C5	506	28.0	.595	47.1
E1	280	13.0	1.00	13.0
E2	347	17.7	1.00	17.7
E3	404	23.0	1.00	23.0
E4	451	32.5	1.00	32.5
E5	507	57.5	1.00	57.5
E6	534	118.5	1.00	118.5

TABLE I (*Concluded*)

No.	Temp.	dp/dt mm./10 min.	P_{Hg}, 0.020 mm I/I_0	dx/dt
G1	287	20.0	1.00	20.0
G2	350	24.0	1.00	24.0
G3	404	31.5	1.00	31.5
G4	452	35.5	1.00	35.5
G5	507	59.5	1.00	59.5
G6	534	112.5	1.00	112.5
J1	235	6.0	0.427	14.1
J2	302	9.0	.427	21.1
J3	360	12.0	.427	28.1
K1	230	8.0	.668	12.0
K2	400	20.0	.668	30.6
K3	440	25.2	.668	37.7
K4	442	25.0	.668	37.4
K5	510	37.0	.668	55.3
K6	512	35.0	.668	52.4
F1	279	9.0	.536	16.8
F2	337	13.0	.536	24.3

of runs was taken as a standard, and other series (made with the same mercury pressure) were correlated with this standard.

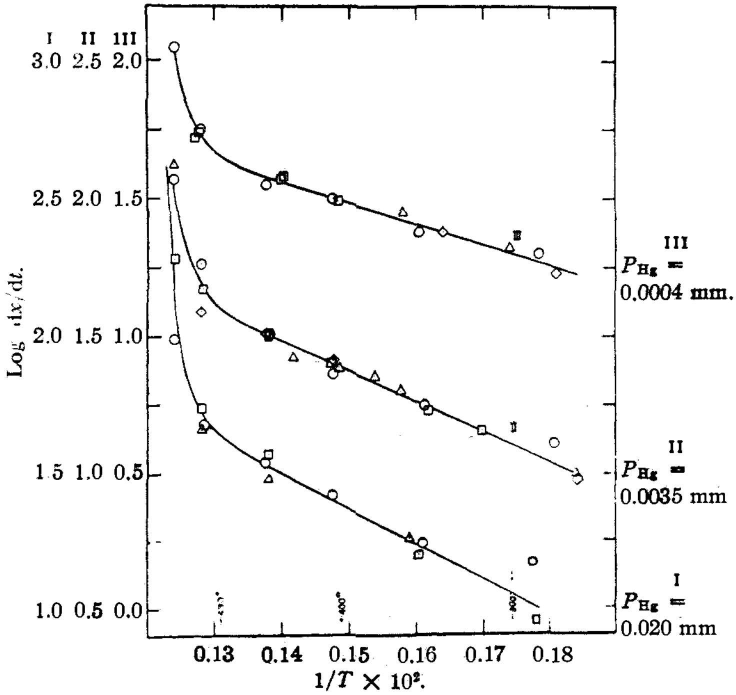

Fig. 1.—Variation of log dx/dt with $1/T$.

A reaction in the dark appeared at temperatures above 490° and amounted in some instances to as much as 25% of the total rate with light. The dark reaction velocity was subtracted from the total velocity in order to obtain the true light velocity.

The data are summarized in Table I, and represented graphically on a log dx/dt–$1/T$ plot, Fig. 1. (The figures under dx/dt were obtained by dividing the values under dp/dt by the ratio I/I_0.)

Discussion

A study of the data presented in the table and the figure reveals the fact that the temperature coefficient of the mercury sensitized hydrogen–oxygen reaction is anti-Arrhenius in character only above 490°. At lower temperatures, the temperature coefficient is small, and follows the Arrhenius law more or less closely. The value of the "constant" E of the Arrhenius equation, calculated from the slope of the curves of Fig. 1, increases from about 3000–5000 calories in the low temperature range to greater than 25,000 calories at high temperatures. The conclusion can, therefore, be drawn that below 490°, the length of the reaction chains does not change sensibly, but that at higher temperatures, the length of the chains increases very rapidly with increasing temperature.

This same conclusion was reached by Kistiakowsky[3] in regard to the direct photochemical reaction. For purposes of comparison with his results, the averaged temperature coefficients, k_{t+10}/k_t have been calculated for the photo-sensitized reaction, and are tabulated in Table II.

TABLE II

TEMPERATURE COEFFICIENT OF HYDROGEN–OXYGEN PHOTOREACTION

Temperature interval, °C.	Photochem. reaction	Mercury photosensitized reaction		
		p_{Hg}, 0.0004	0.0035	0.020
300–400	1.07	1.12	1.09	1.05
400–490	1.13	1.08	1.07	1.05
490–505	1.25	..	..	..
490–510	..	1.17	1.14	1.13
510–530	..	1.37	1.39	1.31

This comparison indicates that a very close agreement exists between the temperature coefficients of the photochemical and the mercury sensitized reactions, and it is reasonable to conclude that the two reactions are practically identical in this respect. Now, Kistiakowsky[3] has shown that the chains produced in both reactions were of approximately the same length at room temperatures. The similarity of the temperature coefficients shows further that the chain lengths are about the same at all temperatures, in spite of the fact that the oxygen atoms initiate the reaction in one case and hydrogen atoms in the other. Such a result is to be expected if the oxygen atoms produce hydrogen atoms by the reaction $O + H_2 = OH + H$, and this would involve that OH radicals do not participate in the chain at least below 490°.

It appears from these results that the mercury sensitized hydrogen-oxygen reaction does not show the characteristics reported by Farkas, Haber and Harteck for the ammonia sensitized reaction. In order to make a direct comparison of the two reactions, a study of the ammonia sensitized reaction was undertaken, using the same apparatus as described above for the mercury sensitized reaction.

The Ammonia Sensitized Reaction.—The ammonia used in the experiments on the ammonia sensitized hydrogen-oxygen reaction was supplied by solutions of ammonium hydroxide contained in a small efficient bubbler cooled in an ice-bath. This method of supplying the ammonia insured a constant partial pressure of both ammonia and water vapor during a run. The source of illumination was a Cooper-Hewitt mercury arc, operated as a hot arc on 3 amperes and 80 volts.

Before presenting the main results and general discussion, one or two observations of interest should be reported.

The Dark Reaction.—When the experiments in this investigation were first commenced, no dark reaction was observable before illumination of the reaction mixture. However, after some fifty separate runs, a slow dark reaction could be detected preceding the light reaction, even at temperatures as low as 300°. When no experiments had been made for several days, on recommencing the runs this dark reaction would not appear for the first few experiments, but, thereafter, would be noticeable in the fresh gas mixtures.

A dark reaction was always observed after every light reaction. For the first minute or two after cutting off the light, the rate of this dark reaction was about 50% of the light rate, but then fell to a very small value. That a dark reaction persisted for a considerable time, however, was shown by permitting a mixture, in which reaction had been initiated previously by light, to stand for several hours in the dark. During this interval a pressure decrease occurred.

The Effect of Mercury.—Since mercury served as the valves and piston of the circulating pump, no attempt was made to remove the mercury vapor from the gases for these experiments with ammonia as a sensitizer. That no sensitization by mercury was taking place was shown by the fact that no reaction occurred in the absence of ammonia when the arc was operated hot. Moreover, the rate of the ammonia sensitized reaction was not affected by varying the partial pressures of mercury from 0.0004 to 0.020 mm. Although this determination was made only for the one partial pressure of ammonia of 14.5 mm., it has been assumed that the presence of mercury has no effect on the reaction rates at other ammonia concentrations.

The Effect of Temperature and of Ammonia Pressure.—Reaction rates for ammonia-oxygen-hydrogen mixtures sensitized to light were measured over a temperature range from 275–450°, and with partial pressure of ammonia from 1.3 mm. up to 97.5 mm. In every case the partial pressures of hydrogen and of oxygen in the system were 400 mm. and 200 mm., respectively. The pressure of water was at all times less than 5 mm.

The graph of an individual reaction indicated that an induction period of one or two minutes existed, after which the reaction proceeded smoothly at a constant speed, measurable by the slope of the straight line portion of the time–dp curve. The reaction rates were quite reproducible, checking within ±4%. Every effort was made to keep the light intensity and other conditions constant during the whole series of experiments, in order that the rates measured at various pressures of ammonia and at various temperatures could be compared directly. That constancy of conditions actually prevailed over a long time was indicated by checking the runs at a given partial pressure of ammonia (14.4 mm.) at intervals during the investigation. The complete data are collected in Table III, showing the reaction rate observed at each temperature and ammonia pressure. Most of the rate values recorded are the mean of two or more duplicate runs. (The values listed under dx/dt were obtained by dividing the figures under dp/dt by the ratio of I/I_0.)

TABLE III

DEPENDENCE OF RATE ON TEMPERATURE AND ON AMMONIA CONCENTRATION

Series letter	NH_3, mm.	Temp., °C.	−dp/dt mm./10 min.	I/I_0	dx/dt
N	1.3	317	2.0	1.00	2.0
		381	1.1	1.00	1.0
		404	3.0	1.00	3.0
		433	2.0	1.00	2.0
		452	6.5	1.00	6.5
K	2.5	272	2.4	1.00	2.4
		324	2.5	1.00	2.5
		355	3.0	1.00	3.0
		381	6.8	1.00	6.8
		404	21.2	1.00	21.2
		422	192.5	1.00	192.5
		433	203.0	1.00	203.0
		435	237.5	1.00	237.5
S	4.8	276	11.9	1.335	8.9
		317	25.5	1.335	19.1
		352	70.5	1.335	52.9
		379	119.0	1.335	89.0
		404	180.0	1.335	134.9
		430	231.0	1.335	173.0
J	5.6	271	6.0[a]	1.00	6.0
		355	70.0	1.00	70.0
		378	95.5	1.00	95.5
		404	151.0	1.00	151.0

TABLE III (*Concluded*)

Series letter	NH_3, mm.	Temp., °C.	$-dp/dt$ mm./10 min.	I/I_0	dx/dt
R	8.9	277	37.0	1.335	27.7
		314	55.7	1.335	41.5
		350	77.5	1.335	58.0
		380	112.5	1.335	84.3
		403	151.5	1.335	113.0
		424	192.0	1.335	144.2
		430	228.0	1.335	170.8
L	9.6	272	6.2[a]	1.00	6.2
		355	55.8	1.00	55.8
		378	83.0	1.00	83.0
		404	122.3	1.00	122.3
T	9.6	275	26.3	1.335	19.6
		314	57.3	1.335	42.9
		351	77.3	1.335	58.3
		380	106.0	1.335	79.4
		404	150.0	1.335	112.4
E	14.5	200	8.0	1.00	8.0
		271	24.3	1.00	24.3
		324	41.0	1.00	41.0
		351	54.0	1.00	54.0
		376	79.0	1.00	79.0
		404	107.7	1.00	107.7
		422	136.0	1.00	136.0
		440	169.5	1.00	169.5
M	31.5	272	13.5	1.00	13.5
		355	38.5	1.00	38.5
		381	57.5	1.00	57.5
		404	83.5	1.00	83.5
I	97.5	271	8.3	1.00	8.3
		355	16.2	1.00	16.2
		378	23.0	1.00	23.0
		404	34.4	1.00	34.4

[a] These abnormally low values for which we have no explanation have been omitted in the graphical representation and in the conclusions drawn from these latter.

The Temperature Coefficient.—A plot of the data of Table III on a log dx/dt–$1/T$ graph, Fig. 2, shows that the reaction velocity of the ammonia sensitized hydrogen–oxygen reaction increases *from 300° upward* more rapidly with temperature than the Arrhenius equation requires. Although this effect is observed with all concentrations of the sensitizer, it is more pronounced when lower partial pressures are employed. The curve obtained with 2.5 mm. of ammonia is particularly striking in this respect.

No explosions were obtained at temperatures up to 435–440°, although the reaction rate was becoming so fast at these temperatures that it seemed likely that explosions might have occurred a few degrees higher.

The Effect of Ammonia Concentration.—The dependence of reaction rate on the concentration of ammonia is indicated in Fig. 3, in which dx/dt is plotted against the partial pressure of ammonia, at three different temperatures. The rate values used in constructing this graph were those read off for the desired temperatures from a graph of the temperature coefficients plotted from all the data of Table III.

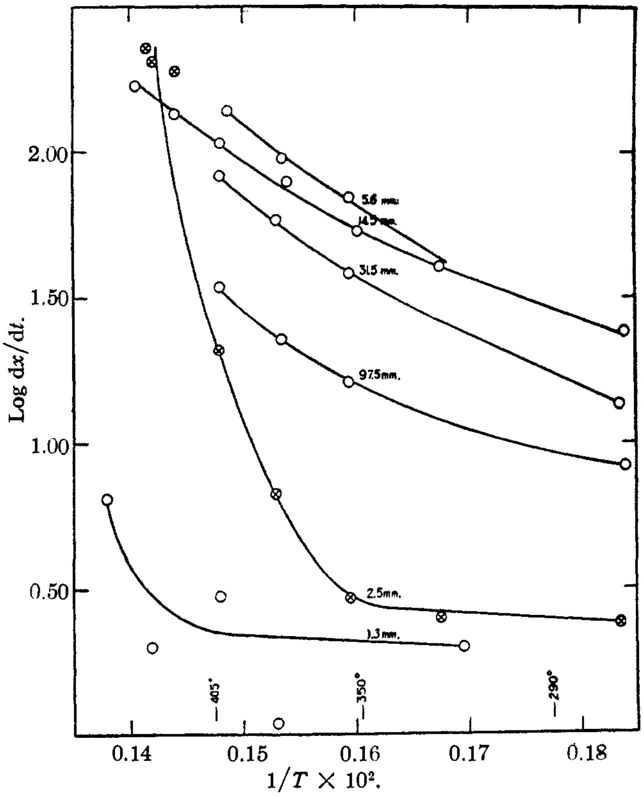

Fig. 2.—Variation of log dx/dt with 1/T.

The curves indicate the remarkable dependence of reaction rate on the ammonia concentration. For any given temperature, there exists a concentration of ammonia at which the reaction rate is a maximum. The interpretation of this fact is that at concentrations of ammonia less than that required to give the maximum rate, the chain propagating influence of ammonia is effective, while at concentrations greater than the optimum, a chain breaking effect of ammonia becomes predominant.

The Chain Length.—In order to estimate the length of the chains occurring in the reaction, the rate of photodecomposition of ammonia was measured. Since this reaction is slow, and since the total volume of the system used for the ammonia sensitized hydrogen–oxygen reaction was large (280 cc.), a direct determination of the ammonia decomposition rate by following pressure change could not be made in that apparatus. Therefore, using the same reaction vessel and furnace, a small static system of total volume of 48 cc. was constructed in which to measure ammonia decomposition. The arrangement of arc, furnace and reaction vessel was the same in this apparatus as in the ammonia sensitized reaction, so that the conditions under which reaction took place were comparable in both cases. The same arc, operating at the identical voltage and amperage, was employed. Tank ammonia, purified by fractional distillation at low temperatures, was used in these experiments.

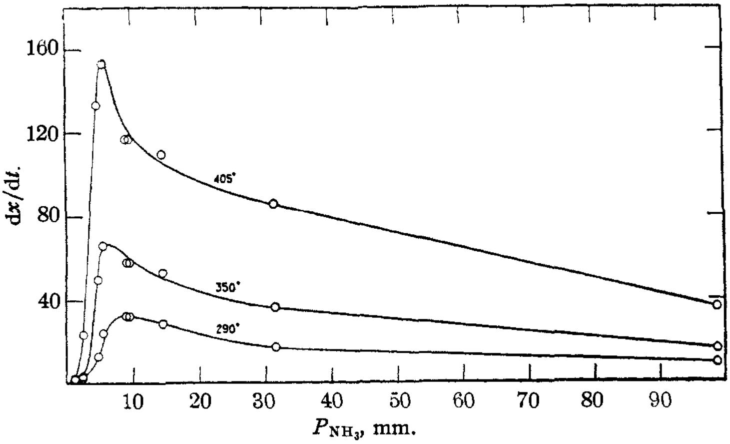

Fig. 3.—Dependence of reaction rate on ammonia pressure.

The rate of the photodecomposition was measured at temperatures from 300 to 450°, and at ammonia pressures from 10 to 100 mm. by following the pressure increase with a constant volume mercury manometer. It was found that the reaction rate fell off as the reaction progressed; consequently the pressure increase occurring in the first two minutes was taken as a measure of the rate of reaction. Also, practically no temperature coefficient was observed for the photodecomposition rate.[10] Consequently, in obtaining the dependence of rate on initial ammonia concentration, the rates observed at the several temperatures were all plotted against the pressure of ammonia. The smooth average curve drawn through all the combined data was of the form $dx/dt \propto I_{abs.} = (1 - e^{-\alpha[NH_3]})$, indicating that the decomposition rate was directly proportional to the ammonia pressure in the low concentration range, and independent of the ammonia pressure at higher concentrations. Complete

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[10] See Wiig and Kistiakowsky, THIS JOURNAL, **54,** 1805 (1932). They find but a slight increase in quantum yield with temperature from 300 to 500°, contrary to Kuhn *Compt. rend.*, **178,** 708 (1924).

absorption was achieved only at fairly high pressures of ammonia, for we were probably dealing only with the weak 2260 Å. ammonia absorption band.

A calculation was then made of the number of moles of ammonia decomposed in unit time in the photodecomposition of ammonia, and compared with the number of moles of water produced in the ammonia sensitized hydrogen–oxygen reaction. The ratio moles of water formed in unit time to moles of ammonia decomposed in unit time should be a measure of the length of the chain existing in the hydrogen–oxygen mixture at a given temperature, assuming that only the hydrogen atoms produced by light from the ammonia are effective in starting chains.[11]

The final figures are collected in Table IV. The first column gives the pressure of ammonia; the second the average number of moles of ammonia decomposed in unit time at any temperature from 290 to 430°; the third, the number of moles of water formed in unit time at 290° in the ammonia sensitized reaction; and the fourth, the ratio of the moles of water formed to the moles of ammonia decomposed. The remaining columns of the table give the corresponding data for the temperatures of 350 and 405°, respectively.

TABLE IV

THE DEPENDENCE OF THE RATIO $\Delta n H_2O/\Delta n NH_3$ ON TEMPERATURE AND AMMONIA CONCENTRATION

		290°		350°		405°	
p_{NH_3}	Av. moles NH_3 decomp. per min. $\times 10^7$	Moles H_2O formed per min. $\times 10^7$	Ratio $\frac{\Delta n H_2O}{\Delta n NH_3}$	Moles H_2O formed per min. $\times 10^7$	Ratio $\frac{\Delta n H_2O}{\Delta n NH_3}$	Moles H_2O formed per min. $\times 10^7$	Ratio $\frac{\Delta n H_2O}{\Delta n NH_3}$
1.3	0.7	...	..	18	25	17	26
2.5	1.3	22	16	24	19	214	115
4.8	2.5	116	47	431	175	1144	460
5.6	2.8	217	76	575	200	1303	504
8.9	4.7	284	59	500	100	1003	210
9.6	5.2	284	55	500	96	1003	194
14.5	7.7	253	33	474	63	876	123
31.5	15.0	151	10	310	21	732	49
97.5	24.1	796	3	205	6	294	13

Discussion

A comparison of the results of our experiments on the mercury sensitized and the ammonia sensitized hydrogen–oxygen reactions indicates that the temperature coefficients of the two do not behave in the same manner, but are in fact quite divergent. However, our findings on the temperature sensitivity of ammonia–hydrogen–oxygen mixtures are essen-

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[11] If the true quantum yield of the ammonia photodecomposition at these temperatures is 0.5, as reported by Kistiakowsky and Wiig, the true chain lengths in the ammonia sensitized reaction should be just one-half of the values reported for the ratio moles water formed to moles ammonia decomposed.

tially in agreement with those of Farkas, Haber and Harteck. This is shown by the following comparative data.

	Farkas, Haber and Harteck	Present work
Total pressure, mm.	500	600
Ratio, $H_2:O_2$	2:1	2:1
Pressure of NH_3, mm.	3	2.5
Molecules water formed per second at 290°	3×10^{17}	5.5×10^{15}
Molecules water formed per second at 405°	2.5×10^{18}	4.5×10^{16}
Ratio $\frac{\text{Molecules per sec. at } 405°}{\text{Molecules per sec. at } 290°}$	8.3	8.2

Our Table IV indicates that the so-called "chain length" is not constant at a given temperature, as it should be, but varies with the concentration of the sensitizer. This is very clearly brought out in Fig. 4, where the ratio moles water formed to moles ammonia decomposed, is plotted against the ammonia pressure. On the low pressure side of the maximum the ratio is dependent almost exactly on the square of the ammonia pressure, while on the high pressure side, the values are inversely proportional to the 1.3 power of the ammonia pressure. The fact that the "chain length" is not constant even at the lower pressures of ammonia, where its inhibiting effect does not enter, indicates the strong influence of the ammonia on the course of the reaction.

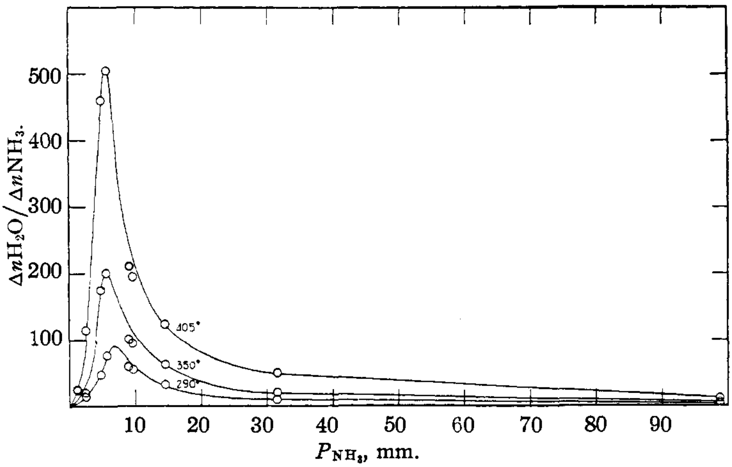

Fig. 4.—Dependence of the ratio, moles of water formed to moles of ammonia decomposed, on the ammonia pressure.

From the facts brought out above, it seems clear that sensitization of hydrogen–oxygen mixtures by ammonia is not simply a case of initiation of reaction by hydrogen atoms. On the contrary, the reaction mechanism must be much more complicated. We suggest as possibilities that NH_2 radicals, and intermediate oxidation products of these, are helping to propagate long chains. It was pointed out some time ago[12] that with oxygen as one of the reactants in the system, there is always the possibility that primary interaction of oxygen with ammonia might influence the course of any reaction in which ammonia was used as a sensitizer. In work with other sensitizers, hydrogen sulfide, hydrogen bromide, etc., for the hydrogen–oxygen reaction, Farkas, Haber and Harteck[13] find that the sensitizer not only produces hydrogen atoms but also enters into oxidation reactions. In preliminary experiments on the photochemical oxidation of ammonia, we find that the rate of removal of ammonia when oxygen is present is three or four times as fast as the photochemical decomposition of ammonia under the same conditions when oxygen is absent. This implies that the photochemical oxidation of ammonia is a chain reaction which may be involved in the mechanism of the ammonia sensitized hydrogen–oxygen reaction. It is known that nitrogen dioxide has an enormous accelerating influence on the explosibility of hydrogen–oxygen mixtures, but evidence indicates that its action may be due to a wall effect. While the possibility of its intervention in the ammonia sensitized reaction cannot be excluded, we incline to the view that the NH_2 fragments are primarily responsible.

As the result of the investigation of the ammonia sensitized reaction, the source of the divergence between it and the mercury sensitized reaction has been located. The appearance of long chains in the ammonia sensitized reaction at temperatures at least 100° lower than the temperature at which they appear in the mercury sensitized or direct photochemical reaction is accounted for by the fact that the ammonia itself powerfully influences the course of the reaction, whereas the mercury has no similar effect.

Since, as is apparent from the preceding considerations, the ammonia and its decomposition products are important factors in determining the length of chain at a given temperature, it is evident that the results obtained from the sensitization experiments with ammonia cannot be used to determine the efficiencies of postulated reactions in the hydrogen-oxygen reaction chain. This has been done by Frankenburger and Klinkhardt, who used the chain length in the ammonia sensitized reaction as a function of temperature as a measure of the activation energy of the reaction $OH + H_2 = H_2O + H$. Had this been correct, the mercury sensitized reaction would have shown a similar temperature variation in the same temperature range. No such is observed. Furthermore, the ammonia concentration markedly affects the temperature variation. No significance attaches, therefore, to the value of 12,000 calories deduced thus for the activation energy, and the arguments based by Frankenburger and Klink-

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[12] Taylor and Emeleus, THIS JOURNAL, **53**, 562 (1931).

[13] Farkas, Haber and Harteck, *Naturwissenschaften*, **18**, 443 (1930).

hardt on this value are correspondingly weakened. This conclusion has been independently reached by Haber and Oppenheimer,[14] who note marked differences between the ammonia sensitized reaction and that initiated by atomic hydrogen from a tungsten arc. While we agree with their conclusion, we believe that their observations with the tungsten arc must be similarly suspect since they show abnormal sensitivity with temperature when compared with our mercury-sensitized and the photochemical reaction. We suspect a reaction accelerated by tungsten dust from the atomic hydrogen arc as the cause of Haber and Oppenheimer's results.

Summary

1. The temperature coefficients of the mercury sensitized and the ammonia sensitized hydrogen–oxygen reactions have been measured at high temperatures.
2. The temperature coefficient of the ammonia sensitized reaction is anti-Arrhenius at temperatures above 300° while that of the mercury sensitized reaction is anti-Arrhenius only above 490°, indicating that a marked increase in chain length occurs at a much lower temperature in the case of ammonia–hydrogen–oxygen mixtures.
3. The temperature coefficients of the mercury sensitized and the direct photochemical reactions of hydrogen and oxygen are shown to be comparable over the whole temperature range. It is suggested that the chain mechanism of the reaction is the same whether initiated by atomic oxygen or atomic hydrogen.
4. The rate of reaction in mixtures of hydrogen and oxygen sensitized by ammonia is markedly dependent on the concentration of ammonia. At low concentrations, a chain propagating influence of ammonia is effective; at high concentrations, a chain breaking effect of ammonia becomes predominant.
5. Sensitization of hydrogen–oxygen mixtures by ammonia is not simply a case of initiation of reaction by hydrogen atoms. It is suggested that NH_2 radicals and intermediate oxidation products of these help to propagate the chains.
6. The cause of the divergence of the ammonia sensitized from the mercury sensitized reaction of hydrogen and oxygen is ascribed to the powerful influence of ammonia on the course of the reaction.

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[14] Haber and Oppenheimer, *Z. physik. Chem.*, **16B**, 443 (1932).