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THE EFFECT OF ADDED GASES ON THE DECOMPOSITION OF AMMONIA SENSITIZED BY OPTICALLY EXCITED MERCURY VAPOR

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Introduction

Experiments such as those of Stuart[1] and Mannkopff[2] on the quenching of resonance fluorescence have shown that the sensitivity of molecules in higher quantum states toward collisions with other molecules is in a highly specific manner dependent on the colliding molecules. Thus, the pressure of added gas necessary to reduce the intensity of resonance fluorescence of mercury vapor by one half was found to be 0.2 mm. for hydrogen, 30 mm. for nitrogen and 240 mm. for argon.

The purpose of the present work was to investigate the effect of argon, nitrogen and hydrogen on the photochemical rate of decomposition of ammonia sensitized to 2537 Å. by mercury vapor. This decomposition had previously been shown by us[3] to be so sensitized; the products of the decomposition, investigated by a quartz-fiber gage, were found to correspond to a mixture of hydrogen and nitrogen containing on the average 70 mole % of hydrogen. The products from the direct photochemical decomposition were found to contain 87 mole % of hydrogen. Results differing somewhat from these were published simultaneously by Taylor and Bates,[4] who showed that the decomposition products contained 89% of hydrogen and 11% of nitrogen for the sensitized, and 96% of hydrogen and 4% of nitrogen for the direct photochemical decomposition. The discrepancies between these results may be due to differences in experimental method. By means of a tartaric acid filter we isolated the sensitized reaction from the direct photochemical decomposition, whereas they apparently did not; we used a static method while they used a flow method. Moreover, the pressures were possibly quite different in the two cases. We have used in the present work the same type of apparatus and procedure as that with which our previous results were obtained. The fact that the ratio of the rate of sensitized decomposition to the direct photochemical rate observed by Taylor and Bates differs from that observed by us is not surprising, since the rate of sensitized decomposition is dependent on the amount of suitable radiation of wave length 2537 Å. used in illuminating the reaction tube.

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[1] Stuart, *Z. Physik*, **32**, 262 (1925).

[2] Mannkopff, *ibid.*, **36**, 315 (1926).

[3] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

[4] Taylor and Bates, *ibid.*, **12**, 714 (1926).

Experimental Procedure

Light from a water-cooled, quartz-mercury arc was allowed to shine on two concentric cylindrical quartz tubes. The inner tube was connected to a mercury-vapor pump and McLeod gage and could be filled with gas at any desired pressure. In a side arm connected to the inner quartz tube was placed about 2 cc. of mercury, in order to give a partial pressure of mercury corresponding to its vapor pressure at room temperature (at which temperature all experiments were made). The total volume of the reacting gas was about 175 cc. The gases ammonia, hydrogen, nitrogen and argon were stored in flasks and could be admitted to the apparatus by means of suitable stopcocks. In the annular space (about 3 mm. thick) between the two quartz tubes a solution could be placed to serve as a light filter.

The filter consisted of a 25% solution of acetic acid. Absorption photographs taken through a thickness of 3 mm. of this solution, using a quartz-mercury arc as a source of illumination, showed that radiation below 2400 Å. was absorbed. It was further found that continued exposure to light from the mercury arc did not change its absorptive power. This was shown both photographically and by the amount of products evolved in a given time from the sensitized decomposition of ammonia, when the acetic acid solution was fresh and after it had been exposed for 30 minutes, the amount of products evolved in a unit time being the same in either case. This has a great advantage over tartaric acid used in previous experiments, since this latter slowly decomposed on illumination and began to absorb in the region of 2537 Å.

The different gases used were prepared as follows. Ammonia manufactured at the Fixed Nitrogen Research Laboratory was dried over soda lime. Before using it in an experiment, however, the amount to be used was condensed in liquid air and the trace of non-condensable impurities remaining was pumped off. Tank (electrolytic) hydrogen was purified by long standing over sodium. Pure nitrogen was prepared by heating sodium trinitride. Argon, obtained from a tank furnished by the General Electric Company, was purified by heating for a number of hours over metallic calcium at about 450°. These gases were all stored in the flasks in which they were purified. Experiments with less carefully prepared nitrogen and argon gave results at variance with those described below, due perhaps to small amounts of oxygen.

The experimental procedure was as follows. After pumping out the reaction system, ammonia was admitted and condensed in the liquid-air trap. After pumping off the non-condensable impurities, the apparatus was closed from the pumps, the liquid air removed, and the ammonia pressure read on the McLeod gage. The ammonia was now exposed to the filtered radiation from the quartz-mercury arc; the arc was water-cooled and a magnet was used to deflect the discharge against the front wall of the lamp. After an exposure of a given length of time, during which a constant current was flowing through the lamp, the cooling water kept at constant temperature, and the level of the water on the lamp at a definite position, the ammonia was condensed by liquid air and the pressure of the residual gases read on the McLeod gage. In case other gases were added together with the ammonia, the procedure was modified in the following way. After measuring the pressure of the purified ammonia, liquid air was replaced at a definite level on the trap, and the ammonia condensed; the added gas was then admitted and its pressure measured on the McLeod gage. The liquid air was then removed, and the ammonia and added gas were allowed to mix thoroughly before illuminating. After illuminating, the ammonia gas was again condensed and the pressure due to the products obtained from the pressure increase measured in the mixture. To measure the effect of added gas, experiments in which added gas was present were compared with those in which ammonia alone was illuminated. Blank experiments on the several added gases were made by exposing them separately to the radiation. Finally, experiments were performed in which ammonia was allowed to decompose in the presence of its own accumulated decomposition products, nitrogen and hydrogen. This was accomplished by radiating the same sample of ammonia for several successive periods of time, the products of the decomposition being allowed to remain in the reaction system.

Experimental Results

The results of the experiments on the effect of argon and nitrogen on the rate of decomposition of ammonia are given in Parts A and B of Table I. With the partial pressure of ammonia at about 3 mm. and that of argon at about 0.3 mm., the rate of decomposition was found to be the same as if there were no argon present. Blank runs with argon at 0.3 mm. showed no change of pressure on being illuminated for the same period of time as in the first experiments (ten minutes). Similar experiments were made using nitrogen as the added gas, with the same results.

Experiments in which hydrogen was used as added gas showed that a few tenths of a millimeter of hydrogen caused a large retarding effect on the rate of decomposition. In these experiments the pressure of ammonia was kept constant at about 3 mm., and that of the hydrogen added varied from 0.0 to 0.3 mm. Blank experiments with hydrogen alone showed a small decrease in pressure corresponding to the "clean-up" of the hydrogen. The results of the experiments are collected in Table I.

Since nitrogen was found to have no effect on the rate of decomposition, and hydrogen was found to have a large inhibiting effect, experiments were made to determine the effect of the products of the reaction on the rate

Table I

Effect of Nitrogen, Argon and Hydrogen on Rate of Decomposition[a]

Time of each illumination, 10 minutes

A. Effect of Nitrogen

Initial press. of NH_3, mm.	Initial press. of N_2, mm.	Final press. of non-cond. gases, mm.	Increase in press. due to products, mm.
3.32	0.000	0.193	0.193
3.32	.303	.497	.194
3.04	.000	.139	.139
3.04	.303	.455	.152
3.31	.000	.116	.116
3.31	.298	.413	.115
3.31	.000	.107	.107
3.31	.298	.412	.114
0.00	.295	.295	.000

B. Effect of Argon

Initial press. of NH_3, mm.	Initial press. of argon, mm.	Final press. of non-cond. gases, mm.	Increase in press. due to products, mm.
3.21	0.000	0.120	0.120
3.21	.309	.462	.153
3.21	.315	.473	.158
3.21	.000	.157	.157
3.26	.000	.145	.145
3.26	.315	.456	.141
0.00	.364	.364	.000

C. Effect of Hydrogen

Intial press. of NH_3, mm.	Initial press. of H_2, mm.	Final press. of non-cond. gases, mm.	Increase in press. due to products, mm.
3.28	0.000	0.188	0.188
3.28	.329	.407	.078
0.00	.330	.320	− .010
3.16	.000	.140	.140
3.16	.313	.366	.053
0.00	.319	.312	− .007
3.29	.000	.121	.121
3.29	.121	.193	.072
0.00	.125	.121	− .004
3.30	.000	.124	.124
3.30	.052	.137	.085
0.00	.043	.040	− .003

[a] In this table, and all following tables, experiments made under comparable conditions of illumination are grouped together, but the illumination for any one group is not necessarily comparable with that for another group.

of decomposition. With a given initial pressure of ammonia in the system, the reaction tube was illuminated for successive periods of time, the ammonia was condensed out after each period and the pressure of the products measured. The ammonia pressure changed only a few per cent. The results of these experiments showed that the products had a marked retarding effect on the rate of decomposition. The data taken from several typical experiments at different ammonia pressures are given in Table II. It will be seen that the amount of products formed per unit time becomes smaller as the average pressure of hydrogen (computed on the assumption that the products are 70% of hydrogen) during the interval becomes greater; also, the depression of the rate of decomposition by hydrogen will be seen to be less, the higher the ammonia pressure.

TABLE II

EFFECT OF DECOMPOSITION PRODUCTS

Initial press. of NH_3, mm.	Total time of illumination, min.	Total press. of products, mm.	Amount of products per minute, mm.	Av. press. of H_2, mm.
0.96	0	0.000		
	5	.025	0.0050	0.0087
	10	.039	.0028	.0223
	20	.062	.0023	.0353
	30	.078	.0016	.0490
1.88	0	.000		
	5	.047	.0094	.017
	10	.080	.0066	.045
	20	.124	.0044	.072
	30	.150	.0026	.096
3.22	0	.000		
	5	.052	.0104	.018
	10	.092	.0089	.050
	20	.148	.0056	.084
	30	.188	.0040	.113
	40	.223	.0035	.144
	50	.248	.0025	.164
5.06	0	.000		
	5	.065	.0130	.022
	10	.122	.0114	.065
	20	.209	.0087	.116
	30	.272	.0063	.168
	40	.322	.0050	.208

Finally, experiments were made to determine how the initial rate of decomposition varied with the ammonia pressure. It was attempted to circumvent the large effect of the decomposition products in the following manner. A sample of ammonia was given several successive illuminations so chosen that the increases in the pressure per unit time were as small as could be conveniently measured. These rates of increase, changing with the pressure of the products, were then extrapolated[5]

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[5] The extrapolation was made by plotting the reciprocal of the average rate for an interval against the average pressure of hydrogen in that interval; the ordinate of this curve at zero hydrogen pressure was taken as the reciprocal of the initial decomposition rate. This method of extrapolation has some theoretical justification; empirically it is convenient, since the curves at low hydrogen pressures are nearly straight lines.

back to zero pressure of the products. Holding the intensity of the illumination as constant as possible, the experiments were repeated at other ammonia pressures. In Table III are given the results of three such series of experiments. In the first series the area exposed to illumination was larger than in the other two. At ammonia pressures of 1 mm. or less the large effect of the products renders extrapolation uncertain; high pressures of ammonia were avoided because of possible broadening of the absorption line of the mercury.

TABLE III

RATE OF DECOMPOSITION AT VARIOUS AMMONIA PRESSURES

Expt. 60 Initial rate, mm./min. × 10^3	Expt. 60 Initial press. of NH_3, mm.	Expt. 61 Initial rate, mm./min. × 10^3	Expt. 61 Initial press. of NH_3, mm.	Expt. 62 Initial rate, mm./min. × 10^3	Expt. 62 Initial press. of NH_3, mm.
5.24	0.955	1.65	1.09	1.23	1.18
9.71	2.10	1.79	1.57	2.24	1.92
13.10	3.60	2.03	2.13	3.57	3.96
18.25	4.69	2.88	3.32	4.06	4.82
		3.31	3.98		
		3.12	4.68		
		4.15	7.40		

Theoretical Discussion of Results

The fact that the addition of 0.3 mm. of nitrogen or argon has no effect on the rate of decomposition of ammonia, while hydrogen at that pressure has a large effect, is in agreement with the work of Stuart[1] mentioned in the introduction.

The effect of hydrogen in strongly decreasing the rate of decomposition is to be explained by the fact that hydrogen, as well as ammonia, can take activation from the excited mercury atoms by collisions of the second kind, the hydrogen thus activated being considered to have no effect on the decomposition. In this case (neglecting complications which might arise from mercury in the $2p_3$ state) we should expect that at sufficiently small ammonia pressures, the pressure of hydrogen required to decrease the rate of decomposition to one-half of the initial value should be the same (about 0.2 mm.) as found in Stuart's experiments or in those of Cario and Franck[6] on the photosensitized reduction of metallic oxides by hydrogen. At higher ammonia pressures, more hydrogen should be required so that values less than 0.2 mm. should never be found. Our data, however, show that considerably lower pressures of hydrogen than this are effective in decreasing the rate to half-value. This indicates that normal hydrogen may take activation from activated ammonia as well as from mercury in the $2p_2$ state; this assumption finds some support in Kuhn's observation[7] that the direct photochemical decomposition

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[6] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

[7] Kuhn, *Compt. rend.*, **178**, 708 (1924).

of ammonia is inhibited by hydrogen. This conclusion is somewhat obscured by the "clean-up" of hydrogen on the walls of the reaction vessel, making the apparent amount of decomposition too small when hydrogen is present; however, from a consideration of Table I C, the amount of "clean-up" is seen to be small compared with the total effect produced by hydrogen. We conclude, therefore, that hydrogen has some other effect beside taking activation from the mercury.

Subsequent to the initial activation of mercury by the absorption of 2537 Å., the following mechanism is accordingly assumed:[8] the activated mercury atom, Hg′, either (1) activates an ammonia molecule or (2) a hydrogen molecule by collision of the second kind, or (3) re-emits the radiation 2537 Å. The activated ammonia, NH_3', either (4) reacts with a normal ammonia molecule, or (5) loses its activation to a hydrogen molecule. The rate of change of (Hg′) is negligible, hence

$$\frac{d}{dt}(\text{Hg}') = K - k_1(\text{Hg}')(\text{NH}_3) - k_2(\text{Hg}')(\text{H}_2) - k_3(\text{Hg}') = 0 \qquad (1)$$

where K is the constant rate of formation of Hg′ and the specific constants k_1 are numbered to correspond to the processes to which they refer. Similarly, the rate of change of (NH_3') is negligible, hence

$$\frac{d}{dt}(\text{NH}_3') = k_1(\text{Hg}')(\text{NH}_3) - k_4(\text{NH}_3')(\text{NH}_3) - k_5(\text{NH}_3')(\text{H}_2) = 0 \qquad (2)$$

The rate of decomposition is then given by

$$R = -\frac{d}{dt}(\text{NH}_3) = k_4(\text{NH}_3')(\text{NH}_3) \qquad (3)$$

Elimination of (Hg′) and (NH_3') gives

$$R = \frac{k_1\, k_4\, K(\text{NH}_3)^2}{\{k_1(\text{NH}_3) + k_2(\text{H}_2) + k_3\}\,\{k_4(\text{NH}_3) + k_5(\text{H}_2)\}} \qquad (4)$$

According to this equation, at constant ammonia pressure, $1/R$ is a quadratic function of the hydrogen pressure; if, however, we had $k_5 = 0$, the function would be linear. Plots of $1/R$ against hydrogen pressure bend upward with increasing hydrogen pressure, affording additional evidence of the dual role of hydrogen in suppressing the decomposition.

By a procedure analogous to that of Turner[9] we may now investigate the efficiency of activation of ammonia by Hg′. In case the pressure of hydrogen is zero we have

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[8] This mechanism makes no provision for the combination of hydrogen and nitrogen to form ammonia; indeed, there seems to be little likelihood that this occurs under the conditions of the experiment [see, for example, Meyer, *Z. Physik*, **37**, 639 (1926)]. The mechanism further takes no account of higher quantum states of mercury than $2p_2$, which might be reached by the absorption of mercury lines other than 2537 Å. by mercury atoms already excited. We have, however, found no increase in the rate of decomposition when the reaction tube was illuminated by an uncooled arc in addition to the cooled arc, using, of course, the acetic acid filter.

[9] Turner, *Phys. Rev.*, **23**, 464 (1924).

$$\frac{1}{R} = \frac{1}{K}\left(1 + \frac{k_3}{k_1(\mathrm{NH_3})}\right) \tag{5}$$

Hence, if the reciprocal of the initial rate is plotted against the reciprocal of the ammonia pressure, a straight line should result, the ratio of whose intercept to slope will be k_1/k_3, the ratio of the specific rate of activation of ammonia by excited mercury atoms to the specific rate of radiation of excited mercury atoms. The three sets of data in Table III give for k_1/k_3 the values 0.200, 0.225 and 0.167 mm.$^{-1}$, or an average of about 0.20 mm.$^{-1}$.

The value of $k_3/k_1 = 5$ mm. is evidently (by Equation 5) the pressure of ammonia at which the initial rate has half the value it would have at large ammonia pressures if no broadening of the absorption line occurred. At this half-value pressure, $(\mathrm{NH_3})_{1/2}$, we have then[10] the rate of activation of ammonia equal to the rate of deactivation of Hg′ by radiation or

$$k_1(\mathrm{Hg'})(\mathrm{NH_3})_{1/2} = k_3(\mathrm{Hg'}) \tag{6}$$

Similarly, for the case of activation of hydrogen by Hg′,

$$k_2(\mathrm{Hg'})(\mathrm{H_2})_{1/2} = k_3(\mathrm{Hg'}) \tag{7}$$

whence, placing $(\mathrm{H_2})_{1/2} = 0.2$ mm. from Stuart's results,

$$k_1/k_2 = (\mathrm{H_2})_{1/2}/(\mathrm{NH_3})_{1/2} = 0.2/5 = 0.04 \tag{8}$$

that is, the specific rate of activation of ammonia by Hg′ is 0.04 of the specific rate of activation of hydrogen by Hg′. This low value is not surprising, in view of the previously mentioned large depressing effect of hydrogen. It receives further qualitative confirmation from comparison of the initial rate of ammonia decomposition with the rate of pressure change in the sensitized hydrogen-oxygen reaction; the latter reaction was found to go the faster even at much lower pressures than were used in the ammonia experiments.

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Summary

Argon and nitrogen at 0.3 mm. pressure have been shown to have little if any effect on the rate of decomposition of ammonia sensitized to the line 2537 Å. by mercury vapor; however, hydrogen at 0.3 mm. and lower pressures has been shown to have a large inhibiting effect on the rate of this decomposition. The rate of decomposition has been found to increase with increasing pressures of ammonia.

The ratio of the specific rate of activation of ammonia to the specific rate of radiation of excited mercury has been estimated to be 0.20 mm.$^{-1}$. From this result the specific rate of activation of ammonia has been calculated to be 4% of the specific rate of activation of hydrogen by excited mercury atoms.

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[10] Stern and Volmer, *Physik. Z.*, **20**, 183 (1919).