[Contribution from the Laboratory of Physical Chemistry of the University of Wisconsin]

THE DECOMPOSITION OF NITROGEN PENTOXIDE IN THE PRESENCE OF FOREIGN GASES

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Received March 14, 1927 Published May 10, 1927

The decomposition of nitrogen pentoxide[1] was for some time the only example of a true unimolecular reaction, but new unimolecular reactions have been discovered,[2] which emphasize the need for a satisfactory explanation of reactions of this type. Molecular collisions as well as thermal radiation have been considered inadequate to account for the observed reaction rates, and attempts have been made recently to explain them on the basis of molecular collisions combined with the changing internal energies of the molecules.[3] Chain reactions[4] have also been advocated to explain the apparent difficulty in obtaining sufficient energy to bring about the reaction.

The nitrogen pentoxide reaction has been studied from a number of angles in this Laboratory in an attempt to obtain experimental facts which may help in the correct interpretation of unimolecular reactions, and the present communication describes the influence of collisions with molecules of a foreign gas.

It has been found that hydrogen, carbon monoxide, bromine and chlorine are without effect on the thermal decomposition of nitrogen pentoxide, but that certain organic vapors bring about a rapid reaction, approaching an explosion. Nitric oxide is oxidized immediately by the nitrogen pentoxide. Hydrogen and air have no effect on the photochemical decomposition but bromine retards it. It has been reported before that nitrogen[5] and oxygen[6] and argon and water vapor[7] are without effect on the decomposition, and that it is affected only slightly by inert solvents.[8]

Experimental Procedure

The apparatus, as shown in Fig. 1, was similar to that used in the first work on nitrogen pentoxide. The glass diaphragm of improved design

[1] Daniels and Johnston, This Journal, **43**, 53 (1921).

[2] (a) The decomposition of acetone [Hinshelwood, *Proc. Roy. Soc.*, **111A**, 245 (1926)]. (b) The racemization of pinene [Smith, This Journal, **49**, 43 (1927)]. (c) The decomposition of azomethane [Ramsperger, This Journal, **49**, 912 (1927)].

[3] (a) Hinshelwood, *Proc. Roy. Soc.*, **113A**, 230 (1926). (b) Thomson, *Phil. Mag.*, [7] **3**, 241 (1927).

[4] Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

[5] Hunt and Daniels, This Journal, **47**, 1602 (1925).

[6] Tolman and White, *ibid.*, **47**, 1240 (1925).

[7] Hirst, *J. Chem. Soc.*, **127**, 657 (1925).

[8] Lueck, This Journal, **44**, 757 (1924).

gave pressure measurements with an error of less than 1 mm. of mercury. The decomposition chamber C was 2.5 cm. in diameter and 78 cc. in volume. The tube A, containing the supply of nitrogen pentoxide, was surrounded by ice in a Dewar flask. The crystals were made by the dehydration of nitric acid with phosphorus pentoxide. The whole system was evacuated through the tubes leading to a high vacuum pump which was protected from corrosion with soda-lime towers.

The bulb B contained the foreign gas which was to be added to the decomposition chamber, and the pressure in B was always greater than in C.

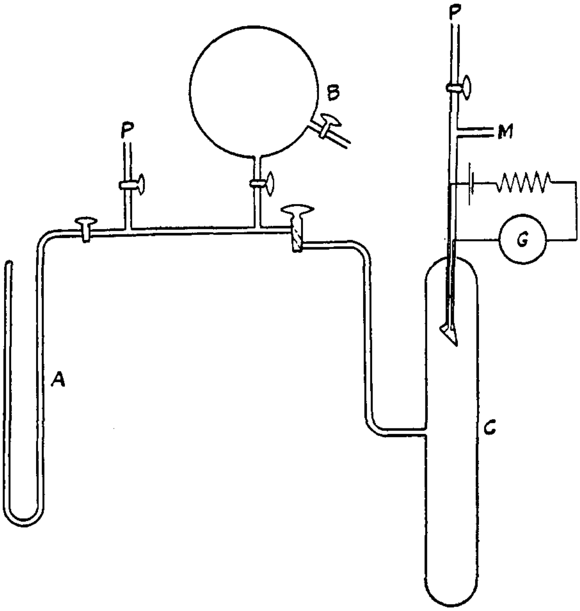

Fig. 1.—Diagram of apparatus.

The thermostat was kept at 45.00°, for at this temperature the decomposition proceeds with a convenient velocity, giving a period of half-life of 23 minutes.[9]

By suitable manipulation of the stopcocks 1, 2 and 3, the decomposition chamber was evacuated, the crystals were purified by partial sublimation and the nitrogen pentoxide gas was distilled into the chamber C after warming the reservoir A. The stopcocks with their coating of vaseline constituted a bad feature of the apparatus but the explosive nature of the gas mixtures prevented the sealing of the chamber. The experiments were so short that no appreciable error was introduced by chemical action on the grease, and experiments with carbon monoxide and hydrogen,

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[9] Ref. 1, p. 70.

continued for 24 hours after the nitrogen pentoxide had decomposed, showed no decrease in pressure.

Pressure readings were taken at frequent intervals and when the decomposition was one-third to one-half completed, the stopcocks were manipulated so as to allow the gas in B to pass over into C. The stopcocks were again closed and the pressure readings taken as soon as possible.

When the pressures P were plotted against the time t, the slopes, dp/dt, gave the approximate reaction rates, neglecting the shifting $N_2O_4 \rightleftarrows 2NO_2$ equilibrium. It is difficult to calculate the true specific reaction rate, for the final pressure cannot be used in the calculation[10] because it is complicated by the addition of the second gas and by the fact that some time is required to adjust the manometer after the addition.

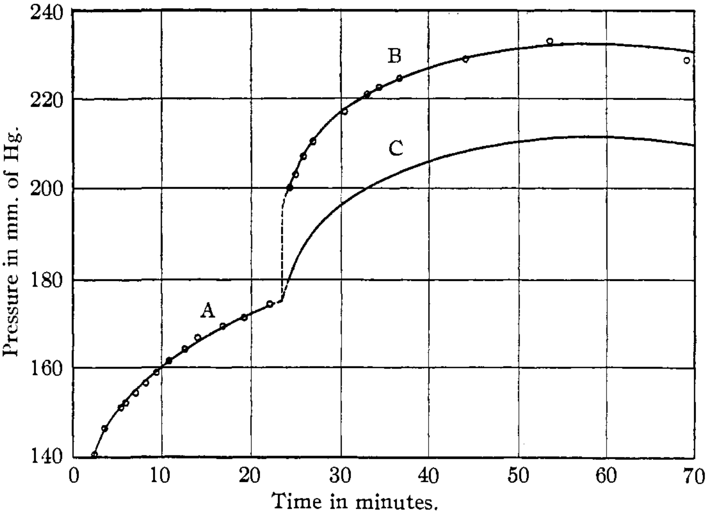

Fig. 2.—Decomposition of nitrogen pentoxide with carbon disulfide at 45°.

The slope of the curve just before and just after the addition of the second gas offers a convenient method for determining whether or not the decomposition rate has been affected. It was estimated that at the pressures used a change of 20% in the reaction rate could be detected with certainty.

The observed pressures for a typical experiment with carbon disulfide are shown at A and B in Fig. 2. The slopes of the two parts of the curve can be compared more easily if they are placed side by side by dropping the curve B to coincide with the lower curve A, as shown at C. The two curves A and B are extrapolated until they cross the ordinate corresponding to the time of addition of the second gas. The intersection of A on this ordinate is then subtracted from the intersection of B and this

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[10] Ref. 1, p. 58.

difference is then subtracted from all the pressures observed along B. In this way the curve C is obtained.

In the photochemical experiments the decomposition chamber was immersed in a thermostat filled with cracked ice and distilled water. The water was agitated with a stream of air and the window was kept free from ice by a wire screen. The condensation of moisture on the outside of the window was prevented by a stream of dry air, but on very humid days the condensed moisture was rendered transparent by means of a soap film.

The light source was a 1000-watt tungsten lamp, operated on the 110-v. circuit and kept at a constant current, usually 8.5 amp., by means of an adjustable rheostat. The distance between the filament and the front of the chamber was 16 cm. and the effective area exposed to the light was 25 sq. cm. A water screen 8 cm. in thickness absorbed most of the heat rays. When the upper part of the chamber containing the diaphragm was covered with tin foil and precautions were taken to prevent the condensation of moisture on the contact points, the diaphragm functioned as well at 0° as at 45°.

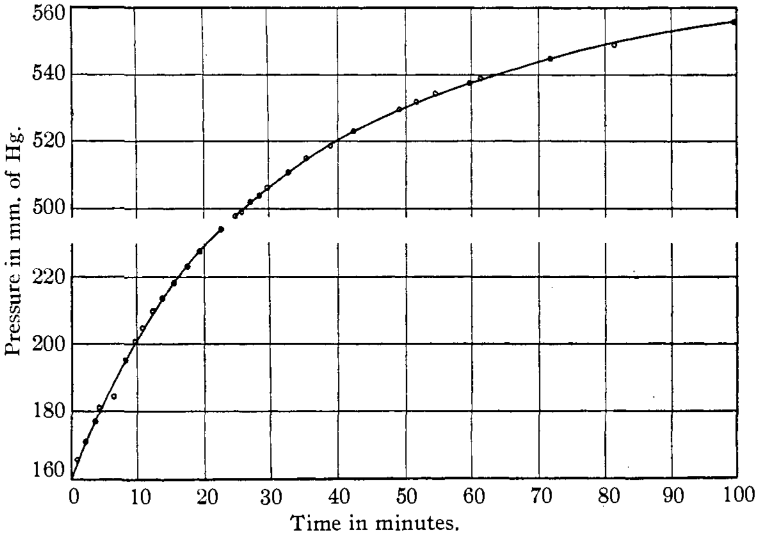

Fig. 3.—Decomposition of nitrogen pentoxide with bromine at 45°.

Thermal Decomposition

Bromine.—When 260 mm. of bromine was added to 160 mm. of nitrogen pentoxide no change in the decomposition rate could be detected, as shown in Fig. 3. The ordinates have been shortened to allow for the addition of the gas and to make the slope easily comparable, as explained for Fig. 2. In all of the experiments, the partial pressure of nitrogen pentoxide was determined approximately by extrapolation on the graph to zero time and the partial pressure of the second gas was estimated from the increase in pressure after opening the stopcock. In a second experiment 340 mm. of bromine had no effect on the decomposition rate of 140 mm. of nitrogen pentoxide.

Chlorine.—No change in the decomposition rate could be detected when 260 mm. of chlorine was added to 180 mm. of nitrogen pentoxide.

Carbon Monoxide.—Two experiments showed no appreciable change in the slope of the pressure-time curve when carbon monoxide was introduced into the decomposing nitrogen pentoxide. In one case the pressures were nitrogen pentoxide, 90 mm., and carbon monoxide, 240 mm., and in the second case they were 105 and 417 mm.

Hydrogen.—Seventeen determinations were made with hydrogen, and the results show conclusively that this gas has no effect on the decomposition of nitrogen pentoxide. Hydrogen, then, is not oxidized by the nitrogen pentoxide. The large number of experiments was necessary because in preliminary work two years before, three curves had been obtained which showed an unmistakable acceleration in the decomposition rate when hydrogen was added. This acceleration could not be duplicated in the present researches and the only explanation seems to be that the tank of hydrogen used at that time must have contained a trace of volatile organic matter.

In the course of the experiments with hydrogen all the possible factors were varied in an unsuccessful attempt to increase the decomposition rate. Various kinds of hydrogen were used, including electrolytic hydrogen from different manufacturers and hydrogen produced by the action of zinc on hydrochloric acid. In some cases the hydrogen was purified with potassium permanganate and alkaline pyrogallic acid, and in others it was used without any purification. In some experiments it was dried with phosphorus pentoxide, in others with calcium chloride, and in others it was not dried at all. In one experiment this hydrogen was mixed with oxygen and ozone, and in another the cell was cleaned thoroughly with concd. nitric acid, an alcohol, and ether. In no case was there evidence of a change in the decomposition rate. The nitrogen pentoxide pressure varied from 100 to 200 mm. and the hydrogen from 5 to 430 mm.

A slight increase in the decomposition rate was produced when emanation from 15 mg. of mesothorium was mixed with the hydrogen.

Nitric Oxide.—Two experiments with nitric oxide showed immediate oxidation. The experiments were arranged so that the oxidation, if it occurred, could be followed by color changes as well as by pressure changes. For this reason the nitrogen pentoxide was introduced into the chamber at 20° and just a few minutes later the nitric oxide was introduced. At this temperature the decomposition was very slow and the chamber was practically colorless. A brown color developed immediately when the nitric oxide was added, indicating that the nitric oxide had been oxidized to nitrogen dioxide by the nitrogen pentoxide. After the addition of the nitric oxide, there was no further increase in pressure even over a period of hours, a fact which showed that all of the nitrogen pentoxide had been reduced. In the first case, the nitric oxide was dried with phosphorus pentoxide and in the second it was saturated with water vapor. In the first case, the partial pressure of nitrogen pentoxide was 100 mm. and the pressure rose to 225 mm. after the addition of nitric oxide. A second addition brought the total pressure up to 450 mm. In the second case, the pressure was increased from 105 mm. to 200 mm. by the addition of the nitric oxide.

In other experiments nitric oxide gas was passed through a cold solution of nitrogen pentoxide in carbon tetrachloride, after first sweeping out all the air. The solution turned brown from the formation of nitrogen dioxide and showed that in solution, also, the nitrogen pentoxide reacts rapidly with the nitric oxide. After an excess of nitric oxide had been passed into the solution and all of the nitrogen pentoxide was destroyed, the solution turned green on account of the union of nitric oxide with the nitrogen dioxide to form nitrogen trioxide.

Carbon Disulfide.—Carbon disulfide vapor has a marked influence on the pressure curve as shown in Fig. 2. In one experiment, when 80 mm. of carbon disulfide was added to 160 mm. of nitrogen pentoxide, the slope of the time-pressure curve increased from approximately 2 mm. per minute to about 6 mm. per minute. In this case the nitrogen pentoxide was about one-third decomposed when the carbon disulfide was added. When the decomposition was nearly complete a second addition of 40 mm. gave only a slight increase in the decomposition rate.

In the second experiment, 22 mm. of carbon disulfide was added to 140 mm. of nitrogen pentoxide after it was about half decomposed, and the rate of the pressure rise increased from 0.9 mm. per minute to 4.4 mm. per minute. After the decomposition was complete, the pressure fell slowly at a rate of about 0.13 mm. per minute for at least four hours. This decrease was observed in most of the experiments with organic vapors and it was probably due to the formation of a liquid phase.

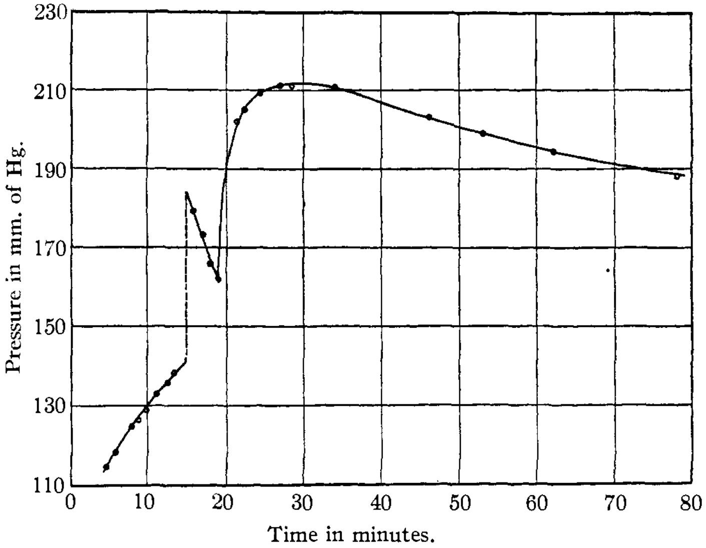

Fig. 4.—Decomposition of nitrogen pentoxide with ether at 45°.

In a third experiment, 200 mm. of carbon disulfide increased the slope from 1 mm. per minute to 2 mm. per minute, but this smaller increase is probably due to the fact that the larger quantity of carbon disulfide caused such a rapid reaction that the major effect was over before the manometer could be adjusted to take the first reading. Two more experiments checked these general conclusions.

Ether.—The experiments with ethyl ether were very complicated but usually interesting. A typical curve is shown in Fig. 4. The first measurements that could be taken after the addition of ether showed a rapidly decreasing pressure, probably due to the formation of an ether-nitrogen pentoxide complex. This decrease was then followed by a rapid rise, almost explosive in nature. After a short time the pressure again decreased, as a liquid phase condensed out from the products of the reaction. The slope of the decomposing nitrogen pentoxide curve was 2.5 mm. per minute, and in two minutes after the addition of ether it had a value of —4.5 and in five minutes a value of +30 mm. per minute.

In a second experiment with an initial pressure of about 130 mm. of nitrogen pentoxide the rate of pressure increase was 1.7 mm. per minute; in two minutes after the addition of 30 mm. of ether vapor the pressure was falling at the rate of 6 mm. per minute and in three minutes it was rising at the rate of 10 mm. per minute.

In a third experiment, with a smaller addition of ether, the curve showed a decreasing pressure of 2.5 mm. per minute followed by a rapid increase of about 10 mm. per minute.

In a fourth experiment at 20°, shown in Fig. 5, the ether was added before any appreciable decomposition had taken place. In this way any possible action between nitrogen dioxide and ether was eliminated.

Several experiments were made with butyl ether, but the vapor pressure of this liquid is so low that it could not be introduced in sufficient quantities for decisive tests.

Acetone.—The curve for acetone is shown in Fig. 6. In this case the decrease in pressure is not followed by an increase. Apparently the acetone-nitrogen pentoxide complex is too stable to decompose under the conditions of the experiment. The latter part of the curve, at least, is accompanied by the formation of a liquid and a crystalline solid in the chamber.

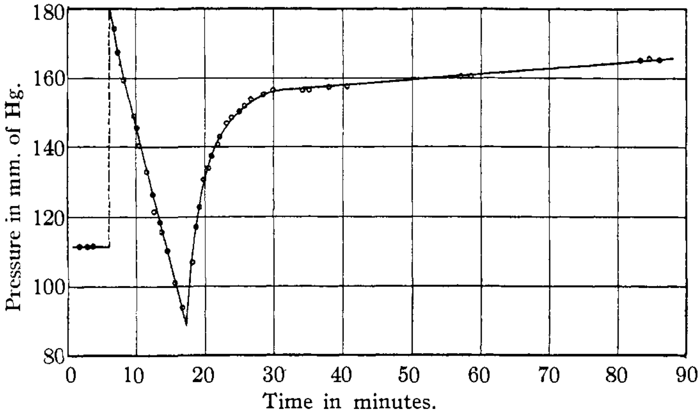

Fig. 5.—Decomposition of nitrogen pentoxide with ether at 20°.

Photochemical Decomposition

Nitrogen Dioxide.—The results of the first work on the photochemical decomposition of nitrogen pentoxide[1] were duplicated and it was found again that nitrogen dioxide is a necessary photocatalyst and that the decomposition increases rapidly at first as the partial pressure of nitrogen dioxide increases, but that further addition of nitrogen dioxide has only a slight effect. The results are shown in Table I, where ΔP/hour gives the increase in pressure per hour at 0°, calculated, usually, from half-hour exposures. The partial pressure of nitrogen pentoxide is maintained at 51 mm. by the presence of the solid crystals.

TABLE I

INFLUENCE OF NITROGEN DIOXIDE CONCENTRATION ON THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN PENTOXIDE

P_{NO_2}, mm.	3	25	48	58	70
ΔP/hour, mm.	2	14	17	23	24

The results are not very accurate because the intensity of the light was not always constant. The decomposition in the dark on standing overnight was usually less than 0.5 mm. per hour, although the ice-bath frequently rose to 4 or 5°.

It was found that more accurate measurements could be made when solid crystals were not present in the cell. It happened that the dimensions of the cell and the intensity of light were such that the increasing concentration of the photocatalytic nitrogen dioxide increased the rate of decomposition only to a slight extent. After the first 3 or 4 mm. of nitrogen dioxide was formed, the pressure increases on illumination were 6, 7 and 8 mm. per hour for three successive one-hour periods. When the illumination was continued another hour the pressure increase was anywhere from 1 mm. to 6 mm., depending on the amount of nitrogen pentoxide left in the cell.

Air.—In Table II the results of the addition of air are given.

TABLE II

INFLUENCE OF AIR ON THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN PENTOXIDE

P_{NO_2}, mm.	23	40	80
P_{air}, mm.	0	67	67
ΔP/hour, mm.	16	20	27

In this experiment the partial pressure of nitrogen pentoxide was kept constant by the presence of the crystals, and a comparison with Table I shows that the photochemical decomposition rate is the same in the two tables within the limits of accuracy of the experiment, for a given partial pressure of nitrogen dioxide.

Experiments in the absence of the crystals showed more conclusively that air does not affect the photochemical decomposition rate. In one case the pressure increased 6 mm. in an hour and after admitting 120 mm. of dry air the pressure increased 5.5 mm. during the next hour. In a second experiment with 424 mm. of air, the pressure rise over three successive hours was 5.5, 7.5 and 8 mm., compared with the 6, 7 and 8 which were found when the nitrogen pentoxide was alone.

Hydrogen.—Two sets of experiments with the solid phase present showed no appreciable change in the photochemical decomposition rate when the partial pressure of the hydrogen was varied from 0 to 364 mm. In the absence of crystals, the pressure increase was 7.5 mm. in the first hour, and 6 and 8 in the second and third hours after adding 75 mm. of hydrogen. In a second experiment, the increase was 7 mm. per hour before the addition of hydrogen and 7.5 mm. afterwards. Within the limits of experimental error, the results are the seme as those obtained without the hydrogen.

Bromine.—Bromine is particularly interesting because its absorption spectrum is similar to that of nitrogen dioxide. Table III gives the results obtained with the solid nitrogen pentoxide present.

TABLE III

INFLUENCE OF BROMINE ON THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN PENTOXIDE

P_{NO_2}, mm.	1	2	20	30	35	73
P_{Br_2}, mm.	0	31	85	85	85	85
ΔP/hour, mm.	2	2	2.7	3.6	4	8

When the concentration of nitrogen dioxide was low and 31 mm. of bromine was added, the decomposition was not increased by light. Bromine, then, is not a photocatalyst for the decomposition of nitrogen pentoxide. Thirty-one mm. of nitrogen dioxide would have given a similar color and would have increased the decomposition rate from 2 mm. to about 15 mm. per hour, as shown in Table I. A further comparison with Table I, at the higher nitrogen dioxide concentrations, shows also that the bromine greatly retards the photocatalytic action of the nitrogen dioxide.

The experiments described in Table IV were carried out to determine the influence of the bromine-nitrogen dioxide ratio.

TABLE IV

INFLUENCE OF THE BROMINE-NITROGEN DIOXIDE RATIO ON THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN PENTOXIDE

P_{NO_2}, mm.	15	25	35	35
P_{Br_2}, mm.	0	0	25	125
ΔP/hour, mm.	14	16	9	3.5

It is evident that the photochemical decomposition decreases as the concentration of bromine increases.

In a third set of experiments the action of bromine was studied in the absence of the nitrogen pentoxide crystals. Whereas the normal decrease in pressure for the third hour should have been 8 mm., as indicated before, in the presence of 25 to 35 mm. of bromine the photochemical decomposition was reduced to 1.5 mm. per hour.

Theoretical Discussion

Nitrogen pentoxide is unable to oxidize hydrogen or carbon monoxide but it is able to oxidize nitric oxide. These facts are not unexpected, for it is known that nitric oxide is oxidized by as weak an oxidizing agent as air, and that hydrogen and carbon monoxide are oxidized at room temperature only with the help of catalysts.

The reaction with nitric oxide is particularly interesting in view of an important suggestion by Norrish concerning the photochemical decomposition of nitrogen pentoxide. According to Norrish,[11] nitrogen dioxide is

[11] Norrish, *Nature*, **119**, 123 (1927).

decomposed by light into oxygen and nitric oxide, and the latter then reacts with nitrogen pentoxide, according to the reactions Light + $2NO_2 \longrightarrow 2NO + O_2$; $NO + N_2O_5 \longrightarrow 3NO_2$. Norrish states in this note that he has experimental evidence for the first reaction, and the present investigation furnishes experimental evidence for the second.

The reaction with nitric oxide seems to clear up certain phases of the thermal decomposition. The reaction has usually been written

$$\begin{tikzcd} 2N_2O_5 \arrow[r] & 2N_2O_4 + O_2 \arrow[d, shift right] \\ & 4NO_2 \arrow[u, shift right] \end{tikzcd}$$

although it has been recognized by everyone that this cannot be the actual reaction, for as written above the reaction is bimolecular rather than unimolecular. The experimental evidence, however, shows conclusively that the rate of the decomposition depends only on the first power of the concentration of the nitrogen pentoxide.

If the unimolecular reaction proceeds in strict accordance with the following equation, nascent oxygen must be produced.

$$\begin{tikzcd} N_2O_5 \arrow[r] & N_2O_4 + O \arrow[d, shift right] \\ & 2NO_2 \arrow[u, shift right] \end{tikzcd}$$

This reaction seems very unlikely on account of the large amount of energy required for the production of *atomic* oxygen.

Bodenstein[12] proposed the following reaction to avoid these difficulties: $N_2O_5 \longrightarrow N_2O_3 + O_2$ (slow); $N_2O_3 \longrightarrow NO_2 + NO$ (fast); $2NO + O_2 \longrightarrow 2NO_2$. At ordinary concentrations, the first reaction is the slowest and therefore it is the one which is measured. Although this theory seemed plausible, it was apparently ruled out by the fact that the specific reaction rate did not change at very low concentrations,[5] where the reaction between nitric oxide and oxygen should have been the slowest reaction.

Christiansen and Kramers[4] suggested two possible chain reactions involving collisions of the second class. According to one hypothesis, nitrogen trioxide and nitrogen pentoxide react to give nitrogen tetroxide. According to the second hypothesis, nitrogen pentoxide reacts with nitrogen dioxide, forming some nitric oxide which then reacts with another molecule of nitrogen pentoxide. According to both hypotheses, the products consist of activated molecules which are able to decompose new molecules of nitrogen pentoxide by collision.

The experimental facts of the present investigation lead to the following proposal which is similar to that of Christiansen and Kramers, and to the other hypotheses described above. $N_2O_5 \longrightarrow NO + NO_2 + O_2$ (slow); $NO + N_2O_5 \longrightarrow 3NO_2$ (fast). The sum of the reactions then is

$$\begin{tikzcd} 2N_2O_5 \arrow[r] & 4NO_2 + O_2 \arrow[d, shift right] \\ & 2N_2O_4 \arrow[u, shift right] \end{tikzcd}$$

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[12] Bodenstein, *Z. physik. Chem.*, **105**, 51 (1923).

These intermediate steps account very satisfactorily for the fact that two nitrogen pentoxide molecules appear as reactants in the stoichiometrical equation, but only one of them is concerned in the kinetics of the reaction. The first molecule is used up in the slow unimolecular reaction $N_2O_5 \longrightarrow NO + NO_2 + O_2$, while the second one reacts rapidly with the reaction products.

According to this mechanism, the number of molecules decomposing in unit time is still proportional to the number present as demanded by the unimolecular reaction rate, but the number decomposing in the slow reaction is only one-half as great as the total number decomposing, as measured by chemical analysis or by pressure changes. The experimentally determined specific reaction rate then should be divided by two in order to obtain the theoretically significant specific reaction rate. The critical increment of 24,700 calories, however, is unchanged.

It is obvious that the nitric oxide produced in the first step might be oxidized by the oxygen, as suggested by Bodenstein. However, the chance that nitric oxide will be oxidized by the nitrogen pentoxide is much greater than the chance that it will be oxidized by the oxygen, even when the oxygen is present in excess. This situation follows from the fact that the nitric oxide concentration is exceedingly small, and the rate of the termolecular oxidation by oxygen depends on the square of the concentration of nitric oxide, while the rate of the bimolecular oxidation by nitrogen pentoxide depends on the first power of the concentration of nitric oxide.

The experiments with organic vapors involve several factors. The increase in the slope of the pressure-time curves may be due to (*a*) an increase in the number of molecules in the reaction products; (*b*) hot regions in the gas produced by the chemical reaction; (*c*) intermediate compounds which then decompose at more rapid rates.

The proper evaluation of these different factors is not easy but it may be pointed out that the reaction is finished sooner when the organic vapors are added, as shown by an extrapolation of the first part of the curve. This fact indicates that the nitrogen pentoxide is decomposed at a faster rate by the addition of the carbon disulfide or the ether, and that it is not merely a matter of the production of more molecules.

The exothermic reactions cannot raise the temperature of the whole gas far enough above that of the thermostat to account for the increased decomposition because the thermal conductance of the gas is good and a temperature rise of many degrees would be required to cause the observed increase in slope.

Although the reaction is slow enough to maintain thermal equilibrium in the ordinary sense, it is true that for brief periods of time the "temperature" of isolated regions may be much higher than the average, and in these regions the decomposition of nitrogen pentoxide may be greatly accelerated. The molecules formed in the exothermic reactions with the organic vapors may give up their extra energy to the nitrogen pentoxide molecules and cause decomposition of the latter if they collide before this energy has been dissipated as heat. The whole field of non-isothermal reactions should be investigated through further studies of this type.

The third suggestion is in accord with the view that the first step in many chemical reactions is the formation of an addition compound, which then dissociates.

Frequently the isolation of the intermediate compound is not possible and the hypothesis in many cases lacks experimental foundation. In the experiments with ether, however, the curve is just what one would expect if the reaction with nitrogen pentoxide is preceded by the formation of an addition compound. The pressure decreases as soon as the ether is added and reaches a minimum value, after which it rises very rapidly. Drops of a liquid were observed soon after the addition.

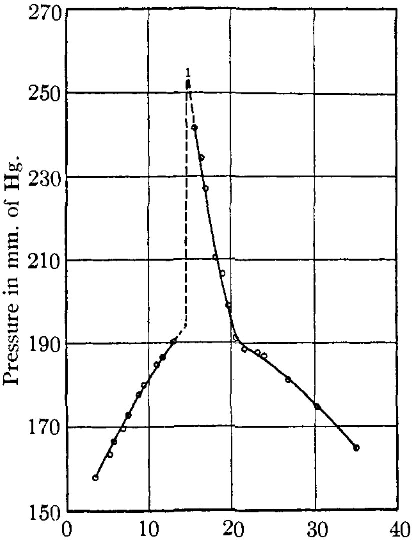

Fig. 6.—Decomposition of nitrogen pentoxide with acetone at 45°.

When crystals of nitrogen pentoxide are added to liquid ethyl ether, the reaction is so violent that the ether catches fire. Under these conditions it would be difficult to isolate the intermediate compound, and the slow gas phase reaction offers many advantages for study. The more inert butyl ether dissolves nitrogen pentoxide without any apparent reaction (unless the nitrogen pentoxide is present in excess), but the nitrogen pentoxide does not decompose in this solvent. Also when small quantities of nitrogen pentoxide are added to liquid acetone, no decomposition of the nitrogen pentoxide can be observed. Probably in these cases an addition compound is formed which is too stable to decompose. The curve of Fig. 6 supports this view. The structures of ether and acetone are such as to lead one to expect an addition compound with nitrogen pentoxide.

With carbon disulfide there is no evidence of an initial decrease in pressure. In this case the carbon disulfide may be oxidized directly by the nitrogen pentoxide without the formation of an intermediate compound, or the measurements may not be adequate for detecting the decrease.

The photocatalytic action of nitrogen dioxide seems to be explained better by the chemical hypothesis of Norrish[11] than by the hypothesis of Fazel and Karrer[13] which is based on collisions of the second class. According to the latter theory, nitrogen dioxide molecules are activated by the absorption of blue light and they are then able to pass over their extra energy to nitrogen pentoxide molecules when they undergo collision. The nitrogen pentoxide molecules, in turn, decompose when they receive this energy.

The experiments described in this communication show that the presence of an inert gas such as hydrogen, or nitrogen or oxygen, does not affect the photocatalytic action of the nitrogen dioxide. It might be expected that the many collisions with the molecules of an inert gas would dissipate some of the energy of an activated molecule of nitrogen dioxide and that the photochemical reaction rate would be decreased. On the other hand, the presence of the inert gas would have practically no effect on the reaction between nitric oxide and nitrogen pentoxide, postulated by Norrish. The experiments cannot be taken to disprove fully the collision theory, however, for the quenching of activated molecules is known to be highly specific, and several collisions may be possible before appreciable loss of energy occurs.

Although bromine absorbs the same light that the nitrogen dioxide absorbs, it is unable to cause the decomposition of nitrogen pentoxide. The fact that bromine destroys the photocatalytic action of the nitrogen dioxide may be explained on the basis of optical screening. Apparently the bromine absorbs part of the light which would otherwise go to the nitrogen dioxide and result in the decomposition of the nitrogen dioxide.

Summary

1. The thermal decomposition rate of nitrogen pentoxide is not affected by collisions with bromine, chlorine, carbon monoxide or hydrogen.
2. Nitric oxide reacts immediately with nitrogen pentoxide.
3. Carbon disulfide gives an increase in the rate of decomposition of nitrogen pentoxide.
4. When ethyl ether is added to decomposing nitrogen pentoxide a decrease in pressure is produced and then a rapid increase.
5. The photochemical decomposition of nitrogen pentoxide in the presence of the photocatalyst nitrogen dioxide is not affected by collisions with oxygen or nitrogen or hydrogen.
6. Bromine cannot be substituted for nitrogen dioxide in the photochemical decomposition of nitrogen pentoxide, even though its absorption spectrum is similar. Bromine decreases the photocatalytic efficiency of nitrogen dioxide probably by screening out the effective light.
7. Theoretical deductions from these facts are discussed.

MADISON, WISCONSIN

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[13] Fazel and Karrer, THIS JOURNAL, **48**, 2837 (1926).