

CXIX.—*The Reactivity of Ammonia.*

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IN a recent paper (Bally and Barker, T., 1921, **119**, 653), some results were described which had been obtained during a quantitative investigation of the photochemical reaction between hydrogen and chlorine. It was found that on exposing the mixture of these two gases to light of various intensities the velocity of union during the first few minutes increases up to a maximum which remains constant. This result has such great significance in relation to modern views of chemical reaction that we undertook some experiments in order to see if a similar result could be obtained in analogous cases. The essential condition for the observation of the phenomenon is the stimulation of an exothermic reaction by the supply of energy at a constant rate, the phenomenon itself being due to the reabsorption by the surrounding molecules of the energy that is radiated during the reaction. A series of measurements was made of the decomposition of nitrous oxide by a platinum wire heated by a constant current. It is sufficient to record the fact that during the first few seconds the velocity of decomposition increases to a maximum, just as in the case of the union between hydrogen and chlorine. When ammonia was substituted for the nitrous oxide, this phenomenon was not observed, but this is to be expected, since the decomposition of ammonia is an endothermic reaction.

In the case of ammonia, the very remarkable fact was noticed that with the platinum wire heated at a constant temperature the amount of decomposition effected in a given time varied very considerably with the velocity with which the sample of gas had been withdrawn from a cylinder of the compressed gas. This phenomenon has been investigated by us in detail, and it is only after eighteen months' work, during which the most rigid tests have been applied, that we now lay our results before the Chemical Society.

The apparatus employed consisted simply of a wide glass tube closed at both ends, with a short piece of stout platinum wire sealed in at each end. A coil of thin platinum wire was attached to these two stout wires and this coil was heated by means of an electric current from accumulators. The glass vessel was provided with an entrance and an exit tube and was filled by passing a stream of ammonia through it. The vessel was completely immersed in a tank through which a constant stream of water was maintained. Since this water came direct from the low-level mains, no appre-

cial variation in temperature took place during a day's work. The decomposition vessel was connected through a tube 0.5 mm. internal diameter and 1 metre long with a delicate manometer filled with xylene. The current was measured to within 0.01 ampere and the time was measured by a quarter-second clock.

The method of experimentation was as follows. The decomposition vessel, after being carefully cleaned and thoroughly dried, was filled with ammonia, and the internal pressure balanced against the atmosphere by means of the manometer. The vessel was then closed by stop-cocks on the entrance and exit tubes, and a known current was passed through the platinum wire for exactly ten or twenty seconds. After sufficient time had elapsed, connexion was remade with the manometer, and the expansion measured, the accuracy of measurement being 0.004 c.c. It is obvious from this method of experiment that any two observations could be made strictly comparable, since, if no change is made in the wire, the passage of the same amount of electricity through the wire for the same time causes a radiation of the same amount of energy to the ammonia in the vessel. This was experimentally confirmed, because with a constant current during a constant time the same sample of ammonia always was decomposed to the same extent, provided no change was made in the wire. For the sake of convenience a series of decompositions of ordinary ammonia was carried out with different currents, the time being the same in each, and from these a curve was drawn. The results obtained with any given current for the same time could at once be checked against this curve.

It has been proved conclusively that constant decomposition values are given by ammonia which has been obtained by slow escape from a cylinder of compressed gas or by gently heating the concentrated aqueous solution. It has also been proved that if the gas from either source is liquefied and allowed to evaporate isothermally at its boiling point, the ammonia thus obtained gives a decomposition value which is identical with that given by the two previous preparations of the gas. It has been previously mentioned that if ammonia is allowed to escape very rapidly from a cylinder containing the liquefied gas, different decomposition values are obtained these being in point of fact much smaller than those given by ordinary ammonia. It was eventually found that when liquefied ammonia is rapidly evaporated, the gas gives a much lower decomposition value than ordinary ammonia.

There is no doubt that this phenomenon is a specific property of the ammonia and that two different types of ammonia can be prepared, an active and an inactive phase. This conclusion has

been definitely established by the following experiments. In the first place, two samples of ammonia can be prepared, one being active and the other inactive. These may be passed alternately into the apparatus and supplied with the same quantity of energy, when high and low decomposition values are alternately obtained. In the second place, if the decomposition vessel is filled with inactive ammonia, and the wire heated at about 200° , the gas after a short time will become active and give a decomposition value which is equal to that of normal or active ammonia. Active ammonia is not affected by this treatment. In the third place, a cylinder full of liquefied ammonia may be taken and by rapid evaporation of the liquid the inactive gas may be obtained. When the cylinder is allowed to remain, the gas left in the cylinder slowly recovers its normal activity, the time for complete recovery depending on the size of the cylinder. With a 15 lb. cylinder, the recovery will be complete within twelve hours, but with a 100 lb. cylinder, the recovery will not be complete until twenty-four hours have elapsed.

We have thus proved that the inactive ammonia becomes normal when allowed to remain for some hours in contact with the liquefied gas, but that in the absence of the liquid it does not recover unless gently heated.

In the following table are given a few results selected at random from amongst the many hundred measurements that we have made.

Type of ammonia.	Current (amperes).	Time in secs.	Expansion in c.c.	Percentage amount decomposed.
Active	4.00	20	0.46	1.00
"	4.10	"	0.65	1.41
"	4.25	"	1.04	2.26
"	4.35	"	1.36	2.96
"	4.50	"	2.16	4.70
Inactive	4.00	"	0.22	0.48
"	4.10	"	0.37	0.80
"	4.25	"	0.65	1.41
"	4.35	"	0.93	2.01
"	4.50	"	1.60	3.48

The difference between the results obtained with the active gas and the inactive gas is very clearly shown. By the measurement of the amount of decomposition when the same sample of ammonia is twice heated, using the same current for the same time in each case, further confirmatory evidence has been obtained, since the ratios between the first and second decompositions are markedly different with the two types of ammonia. In the case of active ammonia the ratio is about 2.6, whilst with the inactive ammonia the ratio is only about 1.5. It is evident from this that in the case of inactive ammonia part of the energy is utilised during the first heating in activating some of the inactive modification. It would

also seem to be established that the two types of ammonia, active and inactive, do not entirely consist of different phases, but that two different phases exist which require different amounts of energy to decompose them and that the active and inactive types differ in the relative amounts of the two phases which they contain. Whilst it is not possible from the measurements we have made to determine the relative amounts present, it appears to be established that the two phases exist, differing in their energy content.

We have also investigated the influence of water vapour on the decomposition of ammonia, and the results we have obtained are of particular interest in their bearing on H. B. Baker's well-known discovery that perfectly dry ammonia does not react with hydrogen chloride. We have found that the addition of water vapour to ammonia very greatly increases the amount of decomposition caused by a definite amount of energy, the increase depending on the amount of water vapour present. We have further proved that ammonia, the activity of which has been increased by the addition of water vapour, loses this increased activity when dried by means of quicklime. The amount, therefore, of the reactive phase present is increased when the ammonia is moist, and is decreased when the ammonia is dried. The suggestion may be made that the amount of the active phase present will still further be decreased by more complete drying, and that, when absolutely dry, ammonia will consist only of the inactive phase. This would offer an explanation of the fact that perfectly dry ammonia does not react with hydrogen chloride, this particular reactivity being a property of our active phase. We endeavoured to obtain the decomposition value of ammonia that had been dried by phosphoric oxide, but we found that the results were vitiated by the presence of volatile phosphorus compounds. It may also be recorded that the decomposition value of ammonia is increased by xylene vapour and other hydrocarbons, although to a less extent than by water vapour. This fact is of some interest, since it is known that such substances cause perfectly dry ammonia to react with hydrogen chloride.

In discussing these results, attention may be directed to the very remarkable differences which have been observed between the absorption spectra of certain substances in the vapour and liquid states. Many compounds, more particularly the nitrogen compounds such as aniline, pyridine, piperidine, etc., show entirely different absorption bands as liquid and vapour. Whatever explanation may be accepted of this, the fact remains that the liquid and gaseous molecules differ from one another. Since this phenomenon has been observed with so many nitrogen compounds, it probably

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also exists in the case of the parent substance, ammonia, and therefore the inactive gas may be assumed to contain more than the normal number of the molecules characteristic of the liquefied gas. Reference may also be made to the fact that when strong sulphuric acid is added to liquefied ammonia no combination takes place between the two liquids, but as the liquid ammonia evaporates, the gas readily combines with the acid. This observation supports the conclusion that the liquid consists of that molecular phase which does not react with acid, and also the deduction that our inactive phase is identical with the non-reactive ammonia prepared by Baker.

It follows from this that the active and inactive forms of ammonia should show different absorption spectra, and we hope to investigate this point. For this purpose, a vacuum spectrograph is necessary, since the absorption band of ammonia lies in the very extreme ultra-violet. Reference may also be made to the conception of gasogen and liquidogen molecules advanced by Traube (*Ann. Physik*, 1902, [iv], **8**, 267). A very interesting result has also been noted by Woltereck (*Compt. rend.*, 1908, **147**, 460) as regards the temperature at which ammonia decomposes. Pure dry ammonia, when passed through a heated glass tube, is not decomposed below 620° , but in the presence of water vapour or organic matter the decomposition begins at a considerably lower temperature. This observation agrees in every way with the experimental results now recorded.

These results conform to the theory of molecular phases put forward by one of us (Bally, *Phil. Mag.*, 1920, [vi], **40**, 15), according to which a molecule, when freshly synthesised, is metastable and at once loses energy and passes into one of a number of possible phases. The energy is lost in terms of the molecular quantum of energy which is a fundamental unit characteristic of the molecule. Each consecutive phase differs in energy content by one molecular quantum and each phase is characterised by a specific reactivity and by an absorption band, the frequency of which is an exact integral multiple of the fundamental molecular frequency. It is possible to change the phase in which a molecule exists by supplying energy to it or by taking energy from it. There are three methods of supplying energy to a molecule and of changing its phase. The energy may be given by a material catalyst, or the molecule may be exposed to long-wave radiation (heat) or to short-wave radiation (light). The increase in reactivity that ensues is due to the change in phase which is produced. In the case of ammonia, the two phases clearly differ in energy content, since a greater amount of energy is required to decompose the inactive phase. They also

differ in reactivity, since the inactive phase is doubtless that phase which Baker found to be incapable of reacting with hydrogen chloride. We do not claim to have prepared either of the two phases in the pure state, but we claim that our results establish the existence of the two phases and explain the want of reactivity of dry ammonia. In view of the present results and the change of molecular phase obtained on drying, it may well be suggested that similar phase changes may be produced on drying other substances. For example, it is to be expected that, if completely dried, aniline, pyridine, and piperidine vapours will be found to consist of the same phase as the liquids.

Finally, we may record some observations on the behaviour of the platinum wire. In our early experiments, a wire was used which previously had been employed in a long series of measurements of the decomposition of nitrous oxide, and it was with this wire that the first observations of the ammonia phenomenon were made. This wire was accidentally fused, and on setting up another apparatus fitted with a piece of the same wire we found that no difference could be detected in the decomposition values of the two types of ammonia. Several kinds of wire were tried, but in each case the result was the same. We found that the wire must be activated in some way, and that this may be effected by alternately heating the wire to 500° and cooling it, this being done at short intervals for several hours. We found also that the wire may be activated in the same way as is necessary in the catalytic oxidation of ammonia in air to nitric acid. A mixture of ammonia and air was passed through the decomposition vessel and the wire was electrically heated to bright redness. After a short time, the electric current being constant, the temperature of the wire began to increase. The current was then decreased little by little, until finally it was found that the wire remained incandescent when the current was stopped. When the wire had been so treated and activated in either of the above ways, the two types of ammonia at once gave the different decomposition values recorded above. Although the wire never loses its activity entirely after it has once been activated, yet the activity falls to a smaller and constant value after long use. The full activity can at once be restored by heating the wire to bright redness for about twenty seconds. Further, a fully activated wire suffers a loss in activity on heating at about 250° for a short time. This peculiar behaviour of the wire led us to investigate most carefully the possibility of our results having been due to the poisoning of the wire, but the evidence we have gained very definitely negatives this possibility. This may be judged from the following summary of our results.

Summary.

1. The decomposition of ammonia by means of a hot platinum wire has been measured.

2. Two types of ammonia may be prepared, an inactive and an active modification, which are decomposed to different extents by the same quantity of energy.

3. The active form is obtained by slow withdrawal of ammonia from a cylinder containing the compressed gas, by warming the concentrated aqueous solution and drying the gas by quicklime, and by isothermal evaporation of the liquefied gas at its boiling point.

4. The inactive form is obtained by rapid evaporation of the liquefied gas.

5. The inactive gas slowly recovers its activity on remaining in contact with the liquefied gas. The same effect can be produced by gently warming the gas by means of a platinum wire heated at 200°.

6. Active and inactive ammonia passed alternately into the same decomposition vessel give with a fixed supply of energy high and low decomposition values.

7. When the same sample of ammonia is twice exposed to the heated wire, the ratios of the amounts decomposed in the two cases differ very materially with the two forms.

8. The addition of water vapour increases the reactivity of ammonia, the increase being proportional to the amount of water vapour present. The enhanced reactivity is removed on drying the gas with quicklime.

9. Two different molecular phases of ammonia exist which possess different reactivities and require different amounts of energy to decompose them. The active and inactive forms of ammonia now described differ in the relative amounts of these two phases which they contain.

10. There is little doubt that the phase of lower energy content is identical with that which is obtained when ammonia is completely freed from moisture and which does not combine with hydrogen chloride.

11. In order to observe these phenomena, the platinum wire must be activated in the same way as is customary in the Ostwald process for the catalytic oxidation of ammonia in air to nitric acid. Alternatively, the activation may be effected by rapidly heating and cooling the wire for several hours.

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