43. *Reaction of Atomic Nitrogen with Solid Acetylene.*

By G. McTurk and J. G. Waller.

Nitrogen atoms, produced by a microwave discharge in nitrogen circulated in a closed system, have been caused to react with solid acetylene at 77° and 90°K. The reaction has a low temperature-coefficient, suggesting a very small activation energy. Measurements of the heat of reaction show that a chain reaction must occur, and this is confirmed by the large amount of polymer produced. The volatile products are hydrogen and hydrogen cyanide. The polymer appears similar to that observed by Versteeg and Winkler among the products obtained from acetylene and atomic nitrogen in the gas phase at higher temperatures.

The reactions of atomic hydrogen with solid, unsaturated hydrocarbons at low temperatures have been studied by Klein and Scheer.[1, 2] These workers developed a technique in which the hydrogen atoms were generated by a hot tungsten filament in a vessel filled with hydrogen gas at low pressure. The unsaturated hydrocarbon was condensed on the walls, cooled usually in liquid oxygen or liquid nitrogen, and the atoms of hydrogen that diffused to the walls reacted. Since the reaction occurred in a static, closed system, its kinetics could be followed by observing the pressure changes. The products were analysed by mass spectroscopy and gas chromatography.

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[1] Klein and Scheer, *J. Phys. Chem.*, 1958, **62**, 1011.

[2] Klein and Scheer, *J. Chem. Phys.*, 1959, **31**, 278; Klein, Scheer, and Waller, *J. Phys. Chem.*, 1960, **64**, 1247; Scheer and Klein, *ibid.*, 1961, **65**, 375; Klein and Scheer, *ibid.*, p. 324.

Production of atoms on a hot filament was convenient since it was clean and reproducible. Experiments by one of the authors (J. G. W.) show that atoms can also be produced by a microwave discharge in the gas, the reaction again being quite rapid. It appears, however, that in these experiments the products are consistently different from those in experiments with the filament. The discrepancy has not been studied.

Further attempts were made to study reactions of nitrogen instead of hydrogen. Clearly, the filament method can no longer be used to produce atoms in high enough yield. When a microwave discharge was struck in nitrogen in apparatus containing nitrogen and solid acetylene, with static gas, no pressure change was observed. However, in other experiments, Broida [3] had observed glows from deposits of acetylene at 4°K when atomic nitrogen condensed on them. Spectra of the glows showed features due to cyanide. In other work at high temperatures Versteeg and Winkler [4] had shown that nitrogen atoms reacted with acetylene.

There were several possible reasons for the failure of the original experiments. First, nitrogen is very much more difficult to dissociate than hydrogen. Shaw [5] has shown that, whereas hydrogen can be virtually completely dissociated, the highest dissociation of dry nitrogen in a microwave discharge is 2—3%. Secondly, the rate of diffusion of nitrogen atoms in the gas may be too small for them to reach the surface in sufficient numbers. And, thirdly, nitrogen atoms may be too big to diffuse in the solid. While Broida's spectroscopic observations appear to contradict the latter suggestion, it is possible that sufficient surface reaction could occur for spectroscopic observation without causing a measurable chemical effect.

To study this problem further, a system was set up in which nitrogen atoms were circulated in a closed circuit over the surface of solid acetylene. The circulation was effected by a mercury diffusion pump, followed by a trap cooled in liquid nitrogen to remove mercury vapour. Since a closed system was used, reaction kinetics could be studied by observing pressure changes. The nitrogen was dissociated in a microwave discharge upstream of the solid acetylene.

APPARATUS AND MATERIALS

The reaction was studied in the apparatus shown in Fig. 1. Nitrogen gas at low pressure was circulated in a closed system by the mercury diffusion pump, through a mercury-vapour trap and a microwave discharge, and over the surface of the solid acetylene at 77° or 90°K. The reaction was followed by observing changes in the pressure, as indicated by the sloping oil-manometer, filled with MS 200 silicone oil of 5 cs. viscosity (purchased from Midland Silicones Ltd.).

The microwave discharge was produced by a Deutsche Elektronik Microwave Therapy unit, which gave a power of up to 400 w at 2450 mc./sec. The microwave power was coupled to the gas by means of a cavity of the type developed at the National Bureau of Standards.[6]

Acetylene from a cylinder was purified by condensing it at liquid-oxygen temperature and pumping to a low pressure at this temperature. The condensed acetylene was then allowed to evaporate into the storage vessel, the first and last portions being discarded. The condensation, evacuation, and evaporation were repeated and the acetylene was then pure.

Two types of reaction vessel were used in these experiments. The original type, used for the first part of the work is shown in Fig. 2. For the later experiments on the effect of distance of the acetylene deposit from the discharge, a simple U-tube was used (as indicated in Fig. 1). For the experiments to measure the heat of reaction, a modified U-tube vessel was used (Fig. 3); part of the U-tube was surrounded by a small jacket which was partly filled with liquid nitrogen; the whole reaction vessel was immersed in liquid nitrogen. The acetylene was condensed in

[3] Broida, personal communication.

[4] Versteeg and Winkler, *Canad. J. Chem.*, 1953, **31**, 129.

[5] Shaw, in Bass and Broida's " Formation and Trapping of Free Radicals," Academic Press, Inc., New York, 1960, Chapter 3; Shaw, General Electric Microwave Laboratory Report No. TIS R 58ELM115.

[6] Broida and Chapman, *Analyt. Chem.*, 1958, **30**, 2049.

the part of the U-tube surrounded by the jacket. Any heat liberated in the reaction then resulted in evolution of nitrogen gas from the jacket and the rate of evolution was measured by a rotameter. Since the whole system was immersed in liquid nitrogen, it is reasonable to assume that the heat liberated was all absorbed in volatilizing nitrogen in the jacket, so that the heat of reaction could be calculated from the known latent heat of evaporation of nitrogen. Control experiments were carried out on the nitrogen evolution when no acetylene was present, and the rate of evolution in these was subtracted from the rate when reaction was taking place.

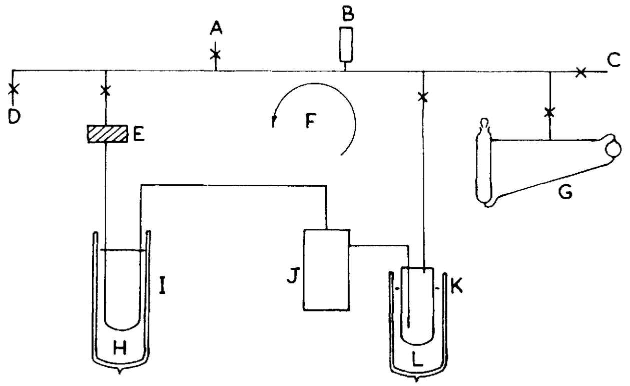


FIG. 1. System for circulation of nitrogen atoms over solid acetylene.

A, From N_2 storage vessel. B, Pirani gauge. C, To high-vacuum system. D, From acetylene storage vessel. E, Microwave discharge cavity. F, Circulation of gas. G, Sloping oil-manometer. H, Liquid O_2 or N_2. I, Reaction vessel. J, Mercury diffusion pump. K, Mercury vapour-trap. L, Liquid N_2. –x– Stopcocks.

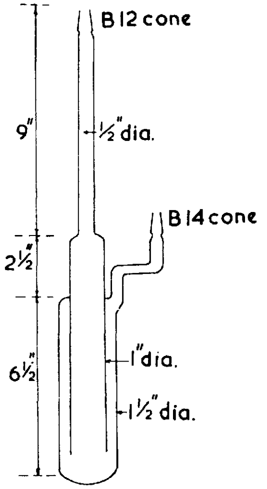


FIG. 2. Original reaction vessel.

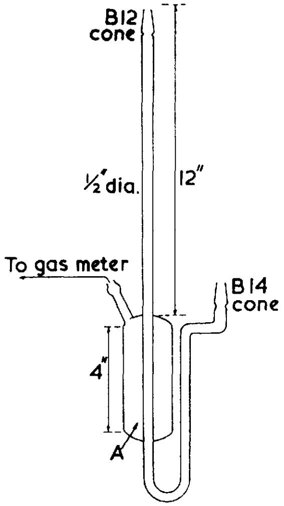


FIG. 3. Vessel for determination of heat of reaction.

A, Liquid-nitrogen jacket, diam. $1\frac{3}{4}$ in.

The volume of the system was measured by observing the change in pressure when a known volume of gas at atmospheric pressure was admitted. With the first reaction vessel, the volume was 1740 ml. and with the U-tube system it was 1620 ml. The rate of circulation could not be measured directly. An approximate measure was obtained by putting enough silicone oil into the mercury trap just to cover the tip of the tube dipping into the trap. The nitrogen circulating in the system then bubbled through the oil. An exactly similar trap was set up alongside and air at atmospheric pressure was bubbled through it. The rate of flow of the air was adjusted to give the same rate of bubbling as in the system at low pressure. The rate of circulation was estimated to be 66 l./hr. Measured at the pressure inside the system and expressed volumetrically, this rate was independent of the pressure, in the range covered (2·0—4·0 mm. Hg), and it was not easily modified by adjusting the heat input to the mercury diffusion pump. The circulation rate at a pressure of 3 mm. Hg corresponds to about 0·25 l./hr. (N.T.P.; 300 mg. of nitrogen per hr.), whilst the total nitrogen in the system during the run is about 8·4 mg.

EXPERIMENTAL

The system was evacuated, and acetylene admitted to a pressure of 17·5 mm. Hg. The acetylene was then condensed in the bottom of the reaction vessel by raising the refrigerant-bath. When all the acetylene had condensed, the refrigerant was raised to a level about 2 in. above the condensate and the system pumped out, before nitrogen was admitted up to a pressure of just over 3·5 mm. The liquid nitrogen was raised to surround the mercury-vapour trap, and the mercury diffusion pump was switched on. The system was left for 10 min. to come to equilibrium and the microwave discharge was then switched on. Readings of the pressure on the sloping oil-manometer were taken every minute until reaction was complete, usually about 20 min. The products were then collected for analysis by pumping off the residual gas, warming the reaction vessel, and recondensing the gas in a refrigerated flask.

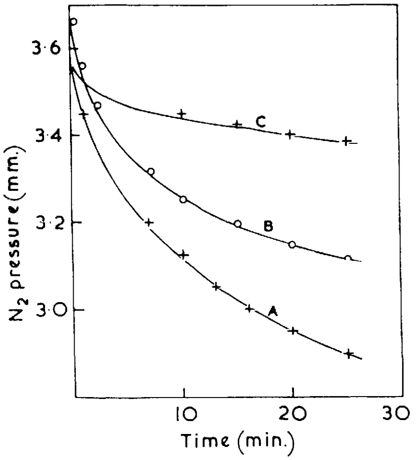


FIG. 4. Rate of reaction of nitrogen atoms with solid acetylene, (A) at 90°, (B) at 77°, and (C) when acetylene is covered with isopentane at 77°K.

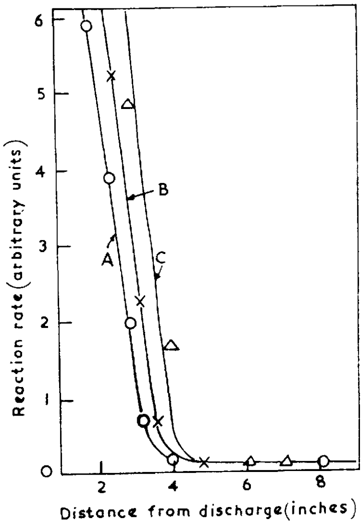


FIG. 5. Effect of distance from discharge on reaction rate. (A) 77°K, coolant raised. (B) 90°K, coolant raised. (C) 77°K, coolant level with deposit.

Results.—The reaction of nitrogen atoms with solid acetylene at 77°K is shown in Fig. 4 as a pressure–time curve for the first reaction vessel (Fig. 2). Quantitative values for the rate of reaction were determined from the slope of the curve at a fixed pressure or by taking the time for the pressure to fall between two predetermined values. The ratios of the rates calculated by the two methods were the same and indicated a very low activation energy of about 0·25 kcal./mole.

When a layer of isopentane ~1·7 μ thick (about 3500 molecules thick) was deposited on top of the acetylene, some reduction in the reaction rate was observed (see Fig. 4). This indicates that the isopentane layer presented a resistance to the diffusion of the nitrogen atoms.

In the study of the reaction of hydrogen atoms with olefins, it was found that a layer of propane up to 1 μ thick deposited on top of the olefin had no effect on the reaction rate, the hydrogen atoms diffusing through it readily.[1]

Dilution of the acetylene with isopentane gave a substantially lower rate, the reduction being far greater than one would have expected for a linear relation between rate and concentration of isopentane. Thus, a 3 : 1 mixture of acetylene and isopentane gave a rate that was about one-third of that for pure acetylene at 77°K.

With the U-tube apparatus, the effect of distance from the discharge could be examined. Acetylene was deposited between 2 and 9 in. from the discharge, and the liquid-nitrogen refrigerant was raised so that the level was well above that of the deposit. The reaction rates at 77° and 90°K are shown in Fig. 5, being expressed as the time for the pressure to fall by a constant amount. The ratio of the rates at 77° and 90°K is virtually the same as in the first reaction vessel.

The results of some further runs, when the refrigerant was raised only as far as the level of the acetylene deposit are also shown in Fig. 5. These rates are higher and it is possible that some of the acetylene was vaporized by the gas from the discharge and that some gas-phase reaction occurred.

Since it is extremely unlikely that sufficient heating could occur in the first vessel (Fig. 2) to vaporize the deposit, it is deduced that in all experiments, except those in which the deposit was level with the surface of the refrigerant, the reaction is between gaseous nitrogen atoms and solid acetylene.

It should be pointed out that during these experiments a change in the discharge characteristics occurred. There appeared to be a reduction in the microwave power available, but the change was not fully understood. For this reason the results for the two types of reaction vessel are not quantitatively comparable.

At the end of an experiment, the residual nitrogen was removed by pumping and the deposit was warmed to vaporize the volatile constituents, which were condensed in a small vessel and analysed. The volatile portion contained mostly hydrogen cyanide and unchanged acetylene. In some runs with the original reaction vessel an unknown, unstable constituent was detected in very small quantities, and there was evidence that this constituent evolved nitrogen during its decomposition. In all attempts to make this compound in the U-tube apparatus, none was detected. After all the runs a brown deposit remained on the walls of the reaction vessel. This material was partly soluble in acetone but not in carbon tetrachloride. It was not soluble in acids or alkalis but could be stripped off the walls with fuming nitric acid or hydrogen fluoride. The nitrogen content of the two fractions of the deposits (*i.e.*, acetone-soluble and acetone-insoluble) were ~10% and ~13%, respectively. The acetone-insoluble fraction, which was by far the greater part of the deposit, has been analysed by infrared spectroscopy as a potassium bromide disc. Although the spectrum could not be interpreted completely, there was very strong evidence for $C{=}C$ and $C{\equiv}N$ linkages. The intensity of the 1650 $cm.^{-1}$ line indicates a chain of conjugated $C{=}C$ groups. Versteeg and Winkler [4] studied the reactions of nitrogen atoms with acetylene in the gas phase and found a similar brown deposit on the sides of the reaction vessel. The deposit could be separated into two fractions, one containing 32% and the other 16% of nitrogen by weight. They were unable to assign a definite structure to the deposit, but they concluded that all the carbon–nitrogen linkages were of the nitrile type.

One experiment was carried out in an attempt to obtain a complete nitrogen balance; at the end of the reaction, the residual gas was removed by pumping, the deposit was warmed to remove the volatile constituents, and these were then condensed in a small vessel in the usual way and analysed. The brown deposit remaining on the wall of the vessel was stripped from it with hydrogen fluoride, the acid was removed by gentle warming, and the deposit was analysed for total nitrogen content. Of the nitrogen that took part in the reaction 65% appeared in the polymer and 25% as hydrogen cyanide. A small amount was found in the volatile fraction of the products and accounted for most of the remaining 10%. This nitrogen is possibly formed by breakdown of some unstable material on warming.

The difficulties of obtaining a satisfactory nitrogen balance can be appreciated if it is remembered that only about a third of the initial 8·5 mg. of nitrogen takes part in the reaction. Much of the 200 mg. of product formed is a somewhat intractable polymer, which is very difficult to remove from the reaction vessel.

In some early experiments with the first reaction vessel, an unstable compound was detected by infrared spectroscopy in the volatile fraction. This material broke down with time and yielded nitrogen. Attempts to isolate it from the remainder of the products failed. It was not possible to reproduce this observation in later work. One possibility, although there is little evidence to support it, is that it is diazoacetylene $CH\equiv C-N=N-C\equiv CH$.

Analysis of the gas remaining at the end of a reaction showed that it contained a very small amount of hydrogen ($\sim$0·1%). No methane was detected.

In the experiments to measure the heat of reaction, a value of about 1500 kcal. per g.-atom of nitrogen that reacted was obtained. This indicates a chain reaction, in accordance with the fact that almost two-thirds of the nitrogen taking part in the reaction appears in the brown polymer.

CHEMICAL MECHANISM

The low energy of activation observed ($\sim$0·25 kcal./mole) is characteristic of free-radical reactions. It is probable that the reactions observed in the gas phase reaction by Versteeg and Winkler [4] are similar to those taking place in our experiments. The large heat of reaction, corresponding to about 1500 kcal. per g.-atom of nitrogen, suggests a chain reaction, which is confirmed by the amount of nitrogen present in the brown polymer. It has not been possible to determine the structure of this polymer completely. However, mechanisms by which the polymer may be formed can be postulated.

The initial reaction is probably

$$\mathrm{N} + \mathrm{CH\equiv CH} \longrightarrow \mathrm{=N-CH=CH-}$$

The radical formed in this reaction may initiate a chain reaction with acetylene molecules:

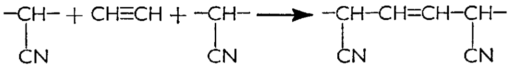
$$\mathrm{=N-CH=CH-} + \mathrm{CH\equiv CH} \longrightarrow \mathrm{=N-CH=CH-CH=CH-}$$

$$\mathrm{=N-CH=CH-CH=CH-} + \mathrm{=N-CH-CH=} \longrightarrow \mathrm{=N-CH=CH-CH=CH-N=CH-CH=}$$

Alternatively, the initial product may lose hydrogen to form a cyanomethylene radical:

$$\mathrm{=N-CH=CH-} \longrightarrow \mathrm{N\equiv C-CH=} + \mathrm{H}$$

This radical would then polymerise with acetylene molecules, thus:



$$\underset{\mathrm{CN}}{\underset{|}{\mathrm{-CH-}}} + \mathrm{CH\equiv CH} + \underset{\mathrm{CN}}{\underset{|}{\mathrm{-CH-}}} \longrightarrow \underset{\mathrm{CN}}{\underset{|}{\mathrm{-CH}}}\mathrm{-CH=CH-}\underset{\mathrm{CN}}{\underset{|}{\mathrm{CH-}}}$$

The latter type of reaction is the more probable, since it accounts for the presence of hydrogen in the residual gas after the reaction has finished, and for the presence of $-C=C-$ and $C\equiv N$ groupings in the polymer. However, it is unlikely that the polymer is as simple as this and there are almost certainly cross-linkages in it. The nitrogen content of $[\cdot CH(CN)\cdot]_n$ is 36% and addition of a further molecule of acetylene, giving a structure $[\cdot CH(CN)\cdot CH{:}CH\cdot]_n$, reduces the nitrogen content to 21%. Polymers containing the observed 10—13% of nitrogen could occur by addition of further acetylene molecules. In this way some conjugation of $-CH=CH-$ units would occur and this would account for other features of the infrared spectrum.

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