The Basic Compound Produced in the γ-Radiolysis of Liquid Nitrogen Containing Hydrocarbons

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Synopsis.   The G-values of the basic compounds produced in the γ-radilysis of liquid nitrogen containing hydrocarbons have been measured by Conway's method. The concentration dependence of the G-values suggests that the basic compounds observed are the products of the reaction between nitrogen atoms and the hydrocarbon radicals eventually formed in the system.

In spite of the considerable number of studies, our understanding of the reactions of nitrogen atoms with hydrocarbons is limited.[1] One of the main reasons is that we have no proper method to produce nitrogen atoms.[2] A few years ago, our laboratory started to use the γ-radiolysis of liquid nitrogen to produce nitrogen atoms.[3] Since small hydrocarbons are soluble in liquid nitrogen, even though the solubilities are not very large, we could investigate a part of the complicated reactions of nitrogen atoms with hydrocarbons. Our concern at that time was mainly with the formation of hydrogen cyanide and nitrile compounds. During these studies, we recognized that there were some other products which were polymeric and basic in nature. We, therefore, tried to measure the G-values of these basic products, our results will be reported below. Unfortunately, however, we are still not successful in identifing these products.

Experimental

The dried high-purity nitrogen was purchased from the Japan Oxygen Co., Ltd., and was used after passing it through sulfuric acid. All the hydrocarbons and hydrochloric acid gas were supplied by the Takachiho Shoji Co. The Nessler reagent was the product of the Kishida Chemical Co.

The samples for γ-irradiation were prepared in almost the same way as has been described before; *i. e.*, the amount of the hydrocarbon is first measured by the *p-v* method, using an oil manometer, and the hydrocarbon is condensed in a glass sampling tube. Then, pure nitrogen is introduced into the tube at 77 K under the pressure a little higher than the atmosphere. The nitrogen is then easily liquified. The amount of the liquid is measured by the scale plotted on the sampling tube. At the top of the tube, a joint is connected by small springs which are easily dislocated if a sudden rise of pressure occurs inside the tube.

The γ-irradiation was carried out in a liquid nitrogen-Dewar flask with the dose rate of 0.65×10^6 R hr^{-1}, usually for one hour.

After irradiation, the sampling tube was again connected to a vacuum system and the inside was slowly pumped out at 77 K. Usually, two hours were taken for complete evacuation. After the evacuation, a small amount of hydrochloric acid gas was introduced into the tube and the tube was warmed up to room temperature. Then, the tube was opened to the atmosphere, and 1 ml of distilled water was

poured into it. The aqueous solution thus prepared was subjected to the following analysis.

If nitrogen-containing products are present in the form of ammonia, amine, or imine, the amount may be measured by Conway's method.[4] A half ml of an aqueous solution is put into the outer section of a Conway vessel, and on the other edge of this section is put 1 ml of K_2CO_3 (30 g ml^{-1}). In the middle section of the Conway vessel, 1 ml of 1/400 M H_2SO_4 is placed. The vessel is then covered tightly with a greased lid and is gently moved in order to mix the product solution and the K_2CO_3 solution. The vessel is warmed in an oven at 38 °C for two hours. After having been cooled to room temperature, the solution in the middle part of the vessel is placed in a 10-ml measuring flask. 1 ml of Nessler reagent is poured into this solution, and then distilled water is added up to 10 ml. When nitrogen-containing products are present, the solution is slightly colored yellow. The absorption of this solution at 430 nm is measured with a Beckman spectrometer against a blank sample exactly 20 min after the Nessler reagent is poured into the solution. The calibration curve was obtained by using ammonia as the test substance. The lowest detectable concentration was 10^{-8} g ml^{-1}.

Results

All of the results are summarized in Fig. 1. From this figure, the following three conclusions may be drawn: 1) The G-values of basic compounds are saturated in the order of the solubilities of hydrocarbons in liquid nitrogen. In the case of ethane, the reported solubility is a 7.8×10^{-3} mole fraction,[5] although this value is not fully reliable.[6] 2) The concentration dependence of the G-values is very similar to that of the G-values of the hydrocarbons produced in the same system, while it is quite different from that of nitrile compounds. One example is shown in Fig. 2. 3)
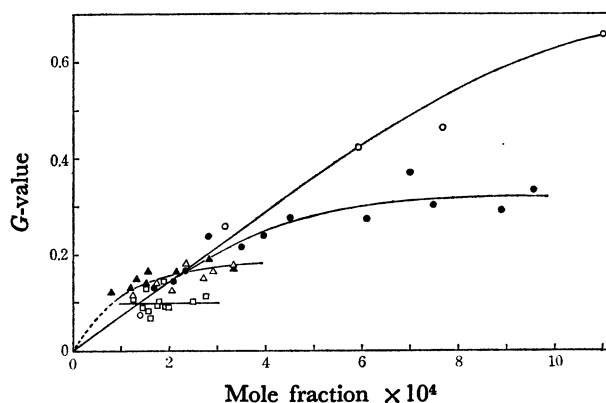

Fig. 1. G-Values of basic compounds as a function of the concentration of hydrocarbons.
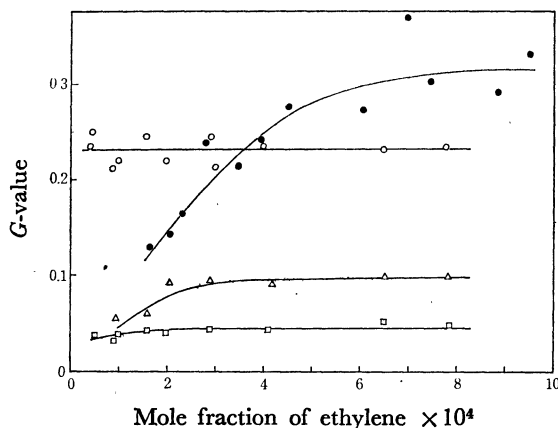O: ethane, ●: ethylene, △: propane, ▲: propylene, □: 1-butene.

Fig. 2. G-Values of hydrogen cyanide (○), acetonitrile (□), acetylene ×10 (△), and basic compounds (●) from the liquid nitrogen solution of ethylene.

At the lowest concentration of hydrocarbons, the rate of formation of the basic compounds is faster for the larger hydrocarbons.

Discussion

In active nitrogen, the lowest excited state of the nitrogen molecule (A $^3\Sigma_u^+$) is known to be long in life (0.9 s). The formation of hydrocarbon radicals in the present system, therefore, may be due to this reaction:
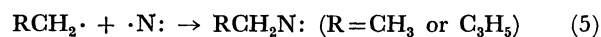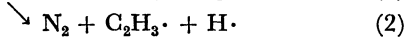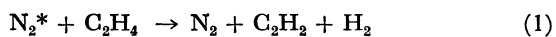
$$N_2^*(^3\Sigma_u^+) + RH \rightarrow N_2 + R\cdot + H\cdot$$
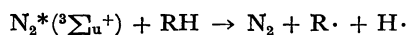
In the case of olefins, the hydrogen atoms thus produced may add to the olefins:

$$R'CH=CH_2 + H\cdot \rightarrow R'CH-CH_3$$
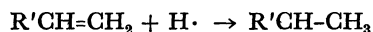
These radicals may react with nitrogen atoms to produce basic compounds.

In the case of ethylene, a possible reaction mechanism for the formation of basic compounds may be described as follows:

$$N_2^* + C_2H_4 \rightarrow N_2 + C_2H_2 + H_2 \qquad (1)$$
$$\searrow N_2 + C_2H_3\cdot + H\cdot \qquad (2)$$

$$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot \qquad (3)$$
$$C_2H_3\cdot + C_2H_4 \rightarrow C_4H_7\cdot \qquad (4)$$
$$RCH_2\cdot + \cdot N\colon \rightarrow RCH_2N\colon \quad (R=CH_3 \text{ or } C_3H_5) \qquad (5)$$
$$RCH_2N\colon \rightarrow RCH=NH \qquad (6)$$

It is well known that an aliphatic imine such as RCH=NH polymerizes at room temperature and is easily hydrolyzed with water to aldehyde and ammonia. In fact, the aqueous solution we obtained in the present experiment showed the silver mirror reaction.

For the formation of nitrile compounds, we previously suggested the following reaction:

$$\cdot N\colon + RCH=CH_2 \rightarrow R\text{-}\overset{\frown}{CH}\text{-}CH_2\cdot \rightarrow RCN + CH_3\cdot \qquad (7)$$
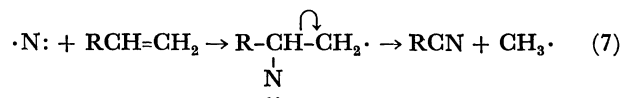
Reaction (7) is obviously compatible with Reactions (1)~(6).

In the case of parafins, however, the reaction mechanism previously proposed for the formation of nitrile compounds[3] is not fully consistent with the mechanism for basic compounds, because the formation of nitrile compounds has also to be attributed to the reaction between nitrogen atoms and hydrocarbon radicals. This apparent inconsistency has not yet been solved. Further studies with different approaches may be necessary.

References

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