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1961

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Abstract

Full Text

Physical Chemistry

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Formation of Hydrazine under the Action of γ-Radiation on Ammonia in the Liquid and Solid States

(Presented by Academician S. S. Medvedev, January 20, 1961)

A change in the phase state of a substance, as is known, is in a number of cases markedly manifested in the course of radiation-chemical reactions. Differences between the gas phase and the liquid phase are well known; differences between the liquid and solid phases have been less studied. However, comparison of the available limited data for processes in these phases—for example, for the radiolysis of hydrocarbons—is made difficult by the fact that these studies were conducted for the most part at different temperatures. Therefore the observed effects could be associated both with differences in the properties of the liquid and solid phases and with differences in the rates of particular stages caused by the temperature difference.

Obviously, the influence of the phase state on the course of radiation-chemical processes is of interest to investigate first of all when the temperature difference is small. It is also essential that the reactions not be highly complex and that it be possible to relate the observed effects to changes in the conditions for particular primary or secondary elementary processes. Such a reaction is the formation of hydrazine upon irradiation of ammonia.

We investigated the formation of hydrazine in liquid and solid ammonia under the action of γ-radiation. Some data, of interest from the standpoint of the special features of the influence of the phase state on the process, are presented in this communication.

Irradiation of ammonia was carried out in quartz ampoules using a Co^{60} γ-radiation source with an activity of $2 \cdot 10^4$ Ci. The radiation intensity was varied within the range 25-790 r/sec. The absorbed energy was determined with a ferrous sulfate dosimeter. The irradiation time ranged from 10 to 10^4 min.

After irradiation, the ammonia was removed by evaporation. Hydrazine was determined by a photocolorimetric method in a hydrochloric-acid solution of *p*-dimethylaminobenzaldehyde. The accuracy of determining hydrazine by this method was on the order of 10^{-1} mg/ml.

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The dependence of the hydrazine yield on temperature is shown in Fig. 1.

With decreasing temperature in the liquid phase, the yield of hydrazine increases. However, upon passing through the freezing temperature of ammonia (-78°), the yield of hydrazine falls; in the solid phase the yield is approximately an order of magnitude smaller than in the liquid phase. Thus, the transition from the liquid to the solid state leads to an abrupt change in the yield of hydrazine. The temperature dependence of the hydrazine yield in the liquid phase corresponds to an activation energy of 3-4 kcal/mol.

The observed influence of the phase state may be explained by a change in the conditions for the formation of $\dot{N}H_2$ radicals.

Apparently, the main reactions leading to the formation of hydrazine are the following:

$$
\begin{aligned}
&1. \quad NH_3 \rightleftarrows \begin{cases} NH_2 + H \\ NH + H_2. \end{cases} \\
&2. \quad NH_2 + NH_2 \to N_2H_4. \\
&3. \quad NH + NH_3 \to N_2H_4.
\end{aligned}
$$

The concentration of NH_2 radicals depends on the process of reverse recombination of hydrogen atoms with their "own" NH_2 radicals. In a liquid, the departure of a hydrogen atom from its "own" NH_2 radical is facilitated in comparison with the solid phase. This, apparently, is one of the reasons for the more effective formation of hydrazine in the liquid phase.

If this explanation is correct, then some acceptor of hydrogen atoms should increase the yield of hydrazine. The action of the acceptor in the solid phase should be stronger than in the liquid phase, since in the liquid phase, owing to the facilitated "departure" of hydrogen atoms in comparison with the solid phase, capture of hydrogen atoms by the acceptor should have less influence on the yield.

Fig. 1. Dependence of the energy yield of hydrazine on temperature. Irradiation time 4 hours. *a*—intensity $1.2 \cdot 10^{16}$ eV/g $\cdot$ sec; *b*—intensity $4.1 \cdot 10^{16}$ eV/g $\cdot$ sec

Fig. 2. Dependence of the energy yield of hydrazine on the molar percent

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of additive in the solid phase. Intensity 200 r/sec. Irradiation time 4 hours. Temperature −80°; *a*—propylene; *b*—propane

We carried out experiments using propylene as acceptors of hydrogen atoms. The results of these experiments are presented in Figs. 2 and 3. In order to eliminate the influence of possible distortions of the solid ammonia lattice by acceptor molecules, experiments were carried out in parallel with additions of the same amounts of propane, which is not an acceptor of hydrogen atoms. From Fig. 2 it is seen that in solid ammonia, with an increase in the amount of propylene, the yield of hydrazine increases. The same amounts of propane do not produce an analogous effect. In liquid ammonia (Fig. 3), addition of propylene does not lead to an increase in the yield of hydrazine.

Thus, the phase effect apparently consists primarily in the fact that the conditions for recombination of H atoms and $\dot{N}H_2$ radicals change. However, the observed effects are probably not completely due only to this cause.

Obviously, differences in the conditions for recombination of $\dot{N}H_2$ radicals with the formation of hydrazine (and also for the reaction of NH radicals with $\dot{N}H_3$ molecules) must also be important. The conditions of the liquid phase are evidently more favorable not only for the formation of $\dot{N}H_2$ radicals, but also for their interaction, since the mobility of these radicals is essential for their recombination. In the solid state such mobility is absent. As some data show, in the solid phase proper the recombination of $\dot{N}H_2$ radicals, and still more the reactions of NH radicals with NH_3, almost do not occur. It should be noted that a lower temperature is also not favorable-

Table 1

	Absorbed energy, eV/g	Number of particles per 1 g NH_3	Energy yield G, particles/100 eV
Formation of radicals	$0.37–0.39 \cdot 10^{21}$	$0.53–0.59 \cdot 10^{18}$	0.14
Formation of hydrazine	$0.35 \cdot 10^{21}$	$0.14 \cdot 10^{18}$	0.038

corresponds to these reactions. This follows from a comparison of the number of radicals, determined by the EPR method in solid ammonia, with the amount of hydrazine formed (Table 1).

As the data presented show, the yield of hydrazine is, in order of magnitude, consistent with the number of trapped radicals. This shows that, at least under these conditions, the reaction in the solid phase practically does not proceed. Apparently, it occurs during the thawing of the irradiated samples, when the particles acquire a certain mobility.

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Fig. 3 graph

Figure 3: Fig. 3 graph

Fig. 4 graph

Figure 4: Fig. 4 graph

Fig. 3. Dependence of the energy yield of hydrazine on the mole percent of additive in the liquid phase. Radiation intensity 200 r/sec. Irradiation time 4 hours. 1 $-t = -70^\circ$; 2 $-t = -35^\circ$. a –propylene, b –propane.

The negative temperature dependence of hydrazine formation in liquid ammonia may be due to various causes. One of them could be the decomposition of hydrazine. Since, at low concentrations of hydrazine, absorption of radiation by the hydrazine molecules themselves is negligibly small in comparison with absorption by ammonia, hydrazine decomposition must occur mainly as a result of interaction with intermediate products of ammonia radiolysis, for example with the radicals NH_2 or NH. Such reactions have a temperature coefficient determined by the activation energy of the interaction of radicals with N_2H_4 molecules and, consequently, with increasing temperature they will be accelerated, which will lead to a decrease in the hydrazine content.

Fig. 4. Dependence of the hydrazine yield on the absorbed energy of γ-radiation. 1 –liquid ammonia, $t = -75^\circ$; a –radiation intensity $1.17 \cdot 10^{16}$ eV/g $\cdot$ sec; b –intensity $4.1 \cdot 10^{16}$ eV/g $\cdot$ sec; for a and b the exposure is varied; v –constant exposure, intensity is varied. 2 –solid ammonia, $t = -196^\circ$; g –radiation intensity $1.17 \cdot 10^{16}$ eV/g $\cdot$ sec; d –radiation intensity $4.1 \cdot 10^{16}$ eV/g $\cdot$ sec; for g and d the exposure is varied.

Consideration shows that the combination of reactions of hydrazine formation (for example, reaction 2) with such reactions of its decomposition leads to a nonlinear dependence of the hydrazine concentration on the energy dose, and at sufficiently large energy doses the concentration of N_2H_4 must acquire a stationary value as a result of the comparison of the rates of its formation and decomposition. However, the experimen-

tal dependences (see Fig. 4) show that, in the range of doses studied, no deviations from linearity are yet observed.

Another possible cause of the negative temperature dependence may be associated with the acceleration of diffusion of NH_2 radicals from the tracks as the temperature is raised, and thereby with a decrease in the probability of their recombination with formation of N_2H_4. Such a mechanism corresponds to a value of the negative effective activation energy on the order of $-3 \div 4$ kcal/mole.

The yield values of about 0.2 molecule/100 eV are, in order of magnitude, in agreement with the value determined earlier by one of us and by E. V. Bolshun and I. A. Myasnikov[1] upon irradiation of liquid ammonia with fast electrons

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(about 0.7 molecule/100 eV).

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Received
20 X 1960

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[1] E. V. Bolshun, S. Ya. Pshezhetskii, I. A. Myasnikov, in: *Action of Ionizing Radiations on Inorganic and Organic Systems*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 184.

Note: Figure translations are in progress. See original paper for figures.

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