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TRANSLATION

THE FORMATION OF HYDRAZINE BY THE ACTION OF Y-RADIATION ON SOLID AND LIQUID AMMONIA

By

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THE FORMATION OF HYDRAZINE BY THE ACTION OF
Y-RADIATION ON SOLID AND LIQUID AMMONIA

Yu. A. Sorokin and S. Ya. Pashehtskiy

As is known, a change in the state of a substance is noticeably manifested in a number of cases during radiochemical reactions. The differences between the gas phase and the liquid phase are well-known, but the differences between the liquid and solid phases are less known. However, it is difficult to compare the available, limited data for the processes in these phases, for example, for radiolysis of hydrocarbons, because these investigations have been carried out for the most part at different temperatures. Therefore, the effects observed could be associated both with the differences in the properties of the liquid and solid phases and with the difference in the rates of these or other stages due to temperature differences.

Evidently the effect of the state on the occurrence of radiochemical processes is interesting to investigate first of all at a small temperature difference. It is also important that the reactions are not complex and that the observable effects can be correlated with a change in the conditions for particular primary or secondary elementary processes. The formation of hydrazine on irradiation of ammonia is such a reaction.

We investigated the formation of hydrazine in liquid and solid ammonia.
Exposed to $\gamma$-radiation, seventeen data are given in this report that are interesting from the point of view of the characteristics of the effect of the state of the process.

Ammonia was irradiated in quartz ampules with a Co$^{60}$-$\gamma$-radiation source with an activity of $2 \cdot 10^4$ curie. The radiation intensity varied between 25 and 790 r/sec. The magnitude of the absorbed energy was determined by a ferrous sulfate dosimeter. The radiation period was from 10 to 104 minutes.

After irradiation ammonia was removed by evaporation. Hydrazine was determined by the photocolorimetric method in a solution of p-dimethylaminobenzaldehyde hydrochloride. The accuracy of determining the hydrazine by this method was of the order of $10^{-1} \text{ mg/ml}$.

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

The hydrazine yield increases with a drop in temperature in the liquid phase. However, the hydrazine yield falls on passing through the solidification point of ammonia ($-18^\circ$); in the solid phase the yield is smaller approximately by one order of magnitude than in the liquid phase. Therefore, the transition from the liquid to the solid state leads to a jumplike change in the hydrazine yield. The temperature dependence of the hydrazine yield in the liquid phase corresponds to an activation energy of $3-4 \text{ kcal/mole}$.

The observed phase effect can be explained by the change in conditions for the formation of NH$_2$ radicals.

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

1. $\text{NH}_2 = \text{NH} + \cdot \text{H}_2$

2. $\text{NH} + \text{NH}_2 \rightarrow \text{N}_2\text{H}_4$

3. $\text{NH} + \cdot \text{NH}_2 \rightarrow \text{N}_2\text{H}_4$

The concentration of NH$_2$ radicals depends on the reverse recombination of hydrogen atoms with "their" NH$_2$ radicals. The moving away of a hydrogen atom
from "its" NH₂ radical is easier in the liquid than in the solid phase. This apparently is one of the reasons for the more efficient formation of hydrazine in the liquid phase.

If such an explanation is valid, then any hydrogen acceptor should increase the hydrazine yield. 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 easier "removal" of the hydrogen atoms as compared with the solid phase, the capture of hydrogen atoms by the acceptor should have a smaller effect on the yield.

We carried out the experiments with propylene as the acceptor of hydrogen atoms. The results of the experiments are shown in Figs. 2 and 3. In order to eliminate the effect of possible distortions of the solid lattice of ammonia by the molecules of the acceptor, experiments were carried out simultaneously with the addition of quantities of propane, which is not a hydrogen acceptor. We see in Fig. 2 that the yield of hydrazine increases in solid ammonia with an increasing amount of propylene.

Thus the phase effect apparently primarily lies in the fact that the conditions for recombination of H atoms and NH₂ are changed. However, the observed effects are probably not due entirely to this cause.

Fig. 1. Energy yield of hydrazine vs. temperature. Irradiation time 4 hr.
a.) intensity 1.2 • 10¹⁶ ev/g • sec;
b.) intensity 4.1 • 10¹⁶ ev/g • sec.

Fig. 2. Energy yield of hydrazine vs. mol. % of addition in solid phase.
Intensity 200 r/sec. Irradiation time 4 hr. Temperature - 80°C; a.) Propylene; b.) propane

Evidently, the difference in the recombination conditions of the NH₂ radicals with the formation of hydrazine (as well as for the reaction of the NH₂ molecules) should also be of importance. The conditions in the liquid phase are apparently...
more favorable not only for the formation of NH₂ radicals, but also for their interaction, since the mobility of these radicals is essential for their recombination. Such mobility is absent in the solid state. As certain data show, in the solid phase proper there is almost no recombination of the NH₂ radicals and even more so, almost no reaction of NH radicals with NH₂. It is necessary to note that a lower temperature also does not promote these reactions. This follows from a comparison between the number of radicals determined by the electron paramagnetic resonance method in solid ammonium and the amount of hydrazine which was formed (Table 1).

| TABLE 1 |
|----------------|----------------|----------------|
|               | Absorbed energy, eV/g | Number of particles per 1 g NH₃ | Energy yield G, particles/100 eV |
| Formation of radicals | 0.37–0.39·10¹⁰ | 0.33–0.39·10¹⁰ | 0.15 |
| Formation of hydrazine | 0.35·10¹⁰ | 0.15·10¹⁰ | 0.008 |

As the data show, the yield of hydrazine corresponds in order of magnitude to the amount of frozen radicals. This shows that at least under these conditions there is virtually no reaction in the solid phase. Apparently it proceeds during thawing of the irradiated samples when the particles acquire a certain mobility.

The negative temperature dependence of hydrazine formation in liquid ammonia can depend on various reasons. One of them could be the decomposition of hydrazine. Since with small concentrations of it, the absorption of radiation by the hydrazine molecules proper is negligible in comparison with the absorption by ammonia, the decomposition of hydrazine should occur mainly as a result of the interaction with the intermediate products of the radiolysis of ammonia, for example with the NH₂ or NH radicals. Such reactions have a temperature coefficient due to the activation energy of the reaction of the radicals with the H₂ molecules and, consequently, the reactions will be accelerated by a temperature rise, which will lead to a decrease in the hydrazine content.
An examination shows that a combination of hydrazine-formation reactions (for example, reaction 2) with such hydrazine-decomposition reactions leads to a nonlinear dependence of the hydrazine concentration on the energy dose, and with sufficiently large energy doses the \( n_2H_4 \) concentration should acquire a steady value as a result of an equalization of its formation and decomposition rates. However, the experimental dependences (see Fig. 4) shows that deviations from linearity are still not observed in the range of the investigated doses.

Another possible cause for the negative temperature dependence can be due to the accelerated diffusion of \( NH_2 \) radicals from the tracks as the temperature increases and thus the probability of recombination with the formation of \( N_2H_4 \) decreases. Such mechanism corresponds to the value of the negative effective activation energy of the order of \(-3-4\) kcal/mole.

Yield values of about 0.2 molecules per 100 ev agree in order of magnitude with the value previously determined by one of us and by Ye. V. Bol'shun and I. A. Myanikov /1/ upon irradiation of liquid ammonia by fast electrons (about FTD-TT-6-833/1*2*4)
0.7 molecules per 100 eV).

References

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