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The Yield of Hydrogen Atoms in the Vapor Phase Radiolysis of Ammonia

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γ-Radiolysis of $NH_3+C_3H_8$ mixtures was investigated at 22 ± 1°C and total pressure $\sim$50 cmHg. From the observed yield of hydrogen, H atom yield of ammonia radiolysis of $G_H=5.1$—5.8 was obtained after subtraction of contribution from the propane fraction. The value is significantly lower than that determined from the study of NH_3+D_2 and $NH_3+N_2H_4$ systems, and also that from the study of $NH_3+C_3H_8$ system reported previously. A variety of possibilities is discussed with respect to the cause of the disagreement. The effect of addition of N_2O or SF_6, which acts as an electron scavenger, was also studied. The yield of hydrogen from $NH_3+C_3H_8$ mixtures decreased appreciably, and $\Delta G(H_2)$ in the absence and presence of electron scavengers was related to the change in the neutralization process.

Similarity in the primary processes of radiation chemistry of ammonia and water has often been recognized although the observed yields of products suggest that the subsequent reactions are different. In the radiolysis of water vapor, there exists a controversy over the primary yield of hydrogen atoms. From the study of isotopic exchange in H_2O+D_2 system Firestone[1] obtained $G_H=11.7\pm0.6$, but using organic compounds as H atom scavengers Baxendale and Gilbert[2] determined $G_H=8.0\pm0.7$. To add another factor to the similarity, two different values were recently reported for the hydrogen atom yield in the radiolysis of ammonia, namely $G_H=12.5\pm1$ by Jones and Sworski[3] from the study on NH_3+D_2 and $NH_3+N_2H_4$ systems, and $G_H\gtrsim7.2$ from that on $NH_3+C_3H_8$ system by Johnson and Smic.[4] Again, the value estimated from isotopic exchange is larger than that with the use of organic scavenger. We have also been investigating the radiolysis of ammonia vapor in an attempt to determine G_H using propane as a scavenger for H atoms. The results we observed are similar to those of Johnson *et al.* However, our interpretation involving the estimation of contribution of propane fraction to the total hydrogen production indicated still another value of G_H which is lower than their value.

Experimental

Ammonia (Matheson, 99.9%), propane (>99.8%), nitrous oxide (99.9%), and sulfur hexafluoride (Matheson, >98%) were purified as described previously.[5] Gas chromatographic analysis using squalane on alumina (4.5 m) of propane thus purified indicated that no organic impurities were present at levels exceeding 10^{-3} mol%.

Irradiations were carried out in glass vessels (about 50 m*l*) fitted with break-seals, baked both in air and at $<10^{-6}$ mmHg before use, in a source of approximately 1000 Ci of ^{60}Co at ammonia pressure of about 50 cmHg and 22 ± 1°C.

Nitrous oxide was used for dosimetry, assuming $G(N_2)=10.0$.[6] The energy absorbed in ammonia (E_a) and in propane (E_p) were calculated using the ratio of stopping powers per molecule obtained by Meisels.[7] The dose rate used was 1.5×10^{16} eV mol^{-1}sec^{-1} in ammonia.

The non-condensable products, hydrogen and nitrogen, were analyzed by combustion in a cupric oxide furnace heated at $\gtrsim$350°C.

Results

Product yields are expressed in terms of G-values calculated for energy absorbed by ammonia, unless otherwise stated. Effect of additives on the product yields are as follows.

Propane. Hydrogen yield steadily increased from $G(H_2)=4.1$ of pure ammonia to 7.8 at 8.6 mol% of propane, while nitrogen yield was markedly depressed (Fig. 1). The increase of hydrogen yield with propane concentration suggests hydrogen production from the direct radiolysis of propane fraction in addition to scavenging H atom from

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3) F. T. Jones and T. J. Sworski, *Trans. Faraday Soc.*, **63**, 2411 (1967).

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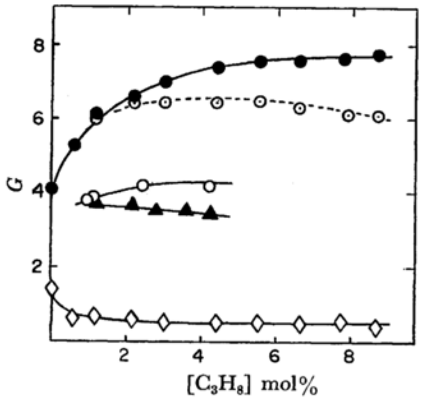

Fig. 1. G-Values of products from $NH_3+C_3H_8$ mixtures.
●, total H_2 from $NH_3+C_3H_8$; ○, H_2 corrected for contribution of C_3H_8 fraction; ○, total H_2 with N_2O ($p_{N_2O}/p_{NH_3}\cong0.05$); ▲, total H_2 with SF_6 ($p_{SF_6}/p_{NH_3}\cong0.005$); ◇, N_2 from $NH_3+C_3H_8$

ammonia, so that correction is necessary. The amount of hydrogen produced from propane fraction was estimated from the energy absorbed in propane taking $G(H_2)=7.5$[8] and assuming absence of energy transfer. The yield of hydrogen corrected in this manner, which is a measure of hydrogen produced in ammonia fraction, is also plotted in Fig. 1. The contribution of propane fraction to the total hydrogen can also be estimated by plotting G-values of total yield (G_t) calculated for the total energy absorbed by the mixture ($E_t=E_a+E_p$) against the fraction of energy absorbed in propane ($f_p=E_p/E_t$). The plot was utilized by Johnson and Simic,[9] and by Jones and Sworski.[3] A good straight-line relationship is demonstrated for lower f_p region where energy transfer between ammonia and propane is negligible, but at f_p higher than 0.15, $G(H_2)_t$ is seen to deviate from the straight line in Fig. 2. Extrapolation of straight portion to $f_p=0$ yields $G(H_2)^\circ=5.84\pm0.05$.

Hydrazine. At the concentration of 5.3 mol%, $G(H_2)=10.0$ and $G(N_2)=7.8$; at 7.4 mol%, $G(H_2)=9.9$ and $G(N_2)=7.6$. They are in fair agreement with the values reported by Jones and Sworski,[3] if converted into $G(H_2)_t$/fraction of stopping power of $NH_3(f_a)$ for comparison.

Sulfur Hexafluoride. $G(H_2)$ decreased from 0.91 at 0.6 mol% to 0.84 at 1.1 mol%, while $G(N_2)$ increased from 2.1 to 2.2.

Propane + Nitrous Oxide or Sulfur Hexafluoride. The effect of addition of N_2O ($p_{N_2O}/p_{NH_3}=0.05$) or SF_6 ($p_{SF_6}/p_{NH_3}=0.005$) to $NH_3+C_3H_8$ mixtures is shown in Figs. 1 and 2. The previous study indicates the concentration of N_2O to be sufficient to scavenge all the electrons produced at the dose rate employed. In Fig. 2, a straight line relationship is demonstrated between $G(H_2)_t$ and f_p in both cases, extrapolation of which leads to approximately the same value, $G(H_2)^\circ\cong3.8$. In order to see if the energy absorbed in the SF_6 in the mixture contributes to the formation of hydrogen, the concentration of SF_6 was varied to $p_{SF_6}/p_{NH_3}=0.016$ at the propane concentration of 3.6 mol%, and to 0.012 at 4.2 mol%. At both concentrations $G(H_2)_t$ increased by about 10%, indicating the presence of small contribution. It is tentatively assumed that the contribution is negligible at $p_{SF_6}/p_{NH_3}=0.005$. $G(N_2)$ is depressed from 9.8 of NH_3+N_2O (100 : 5) to 3.5 by the addition of C_3H_8 (1—3 mol%) to NH_3+N_2O mixtures.

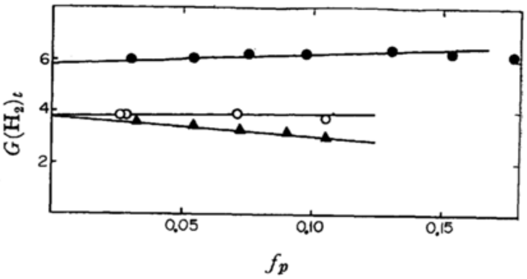

Fig. 2. Dependence of $G(H_2)_t$ on the fraction of energy absorbed by C_3H_8 ($f_p=E_p/E_t$).
●, from $NH_3+C_3H_8$; ○, with N_2O($p_{N_2O}/p_{NH_3}\cong0.05$); ▲, with SF_6 ($p_{SF_6}/p_{NH_3}\cong0.005$)

Discussion

Hydrogen atoms react with propane by

$$H + C_3H_8 \rightarrow H_2 + C_3H_7 \qquad (k\sim2\times10^6\,\mathrm{M}^{-1}\cdot\mathrm{sec}^{-1})^{10)} \qquad (1)$$

Charge and proton transfer from NH_4^+, which is the principal ionic species in the radiolysis of ammonia,[11] to propane can be excluded on the energetic grounds because of the low ionization potential for NH_4,[12] and the high proton affinity of NH_3,[13] while on the same ground transfer from $C_3H_8^+$ to NH_3 can occur. The hydrogen yield from the radiolysis of $NH_3+C_3H_8$ mixtures may be composed of the "molecular" hydrogen from ammonia (A), that produced through reaction (1) by H atoms formed in ammonia (B), and that produced in propane fraction (C). In order to estimate the contribution of propane fraction to the hydrogen yield, it is necessary to determine the extent of energy transfer between propane and ammonia. Since this cannot be accomplished from the product analysis without the use of isotopically

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[10] H. A. Kazmi, R. J. Diefendorf and D. J. Le Roy, *Can. J. Chem.*, **41**, 690 (1963).

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[12] C.E. Melton and H. W. Joy, *ibid.*, **46**, 4275 (1967).

[13] A. P. Altschuller, *J. Am. Chem. Soc.*, **77**, 3480 (1955).

labeled additives, two methods were used as the zeroth approximation, both assuming energy transfer being negligible at lower concentration range of propane. One of the methods is simply to subtract the yield of hydrogen calculated for energy absorption in propane from the total yield. A narrow range of plateau in $G(H_2)$ is seen in Fig. 1, which should be a measure of (A)+(B), *i. e.*, $G_H+G_{H_2}=6.5$. The other method is based on the equation

$$\begin{aligned} G(H_2)_t &= G(H_2)_a^\circ \cdot f_a + G(H_2)_p^\circ \cdot f_p \\ &= G(H_2)_a^\circ + [G(H_2)_p^\circ - G(H_2)_a^\circ] \cdot f_p \qquad (1) \end{aligned}$$

where G_a° and G_p° are those due to energy deposited in ammonia and in propane, respectively, and f_a and f_p are the fraction of energy absorbed by ammonia and by propane in the mixture, which is given by $f_a=s_a[NH_3]/(s_a\cdot[NH_3]+s_p\cdot[C_3H_8])$ where s is the relative stopping power per unit concentration.[7] At the lower f_p region the plot of $G(H_2)_t$ *versus* f_p demonstrates a sufficiently straight line in Fig. 2, which, according to Eq. (1), indicates that the assumption may be justified. The intercept, $G(H_2)_a^\circ=5.84\pm0.05$, should then be another measure of $G_H+G_{H_2}$ of ammonia. The slope of the straight line gives $G(H_2)_p^\circ=10.4$; the value determined by Johnson and Warman is 7.5.[8] $G_{H_2}=0.74$ of ammonia radiolysis determined earlier[5] is in excellent agreement with 0.75 reported by Jones and Sworski[3] and with <0.8 by Johnson and Simic.[4] It follows that the value of G_H lies in the range of 5.1 to 5.8, which is significantly lower than those reported by Jones and Sworski and by Johnson and Simic. It is not obvious whether due corrections were made to the contribution of propane fraction to hydrogen yield by Johnson and Simic. If not, the neglect of (C), could account for most of the disagreement with their value. It is also possible that the disagreement is due to difference in the dose rate used (their dose rate is higher by a factor of 100), although it is not altogether clear how it should affect the yield in ammonia-propane system. The more serious disagreement with Sworski's value might be, at least in part, inherent in the system they used. For example, with the NH_3+D_2 system they observed G_H as high as 90 ± 66 at the ammonia pressure of 600 Torr by a fairly complicated kinetic analysis using a variety of parameters. High G-values are usually attributed to some kind of chain mechanism. In fact, very high G(HD) observed at 200°C is explained in terms of a chain mechanism involving D atoms. Since $G_H=90$ was determined at 24°C, the mechanism would probably include ionic species, if chain reactions are to be invoked. Some ambiguity, therefore, still remains in $G_H=12.5\pm3.0$ at 200 Torr.

In $NH_3+N_2H_4$ system, H_2 is considered to be formed from H atoms as precursors mainly by the reaction $H+N_2H_4\rightarrow H_2+N_2H_3$,[3] as well as a minor fraction of "molecular" H_2. Johnson and Simic observed that $G(H_2)$ of $NH_3+C_3H_8$ system is independent of temperature over the range 20—200°C at around 8.0, while that of pure ammonia increases to $G(H_2)\cong15$ at 200°C. Similar results in the pure ammonia were observed by Jones and Sworski. Our results on the $NH_3+C_3H_8$ system at high densities ($d \sim 0.1$ g/m*l*) and 140°C also indicate a constant $G(H_2)$ independent of temperature and density.[14] Since the marked depression of $G(N_2)$ by propane, observed by Johnson and also in the present work, suggests scavenging of precursors of nitrogen,

$$NH_2 + C_3H_8 \rightarrow NH_3 + C_3H_7 \qquad \Delta H = -9\text{—}11\ \text{kcal/mol} \qquad (2)$$

the difference in the hydrogen yield between pure ammonia and $NH_3+C_3H_8$ at elevated temperatures could be accounted for by hydrogen formation from intermediates other than H atoms which is favored at higher temperatures. At low temperatures reactions conceivable for H and NH_2 include:

$$H + H \rightarrow H_2 \qquad (3)$$

$$H + NH_2 \rightarrow NH_3 \qquad (4)$$

$$H + NH_3 \rightarrow NH_2 + H_2 \qquad (5)$$

$$NH_2 + NH_2 \rightarrow N_2H_4 \qquad (6)$$

$$H + N_2H_4 \rightarrow H_2 + N_2H_3 \qquad (7)$$

$$NH_2 + N_2H_4 \rightarrow NH_3 + N_2H_3 \qquad (8)$$

Reaction (5) is unimportant at ~20°C because of the activation energy of 10—15 kcal/mol,[15] while it certainly is favored at elevated temperatures, resulting in the enhancecment of NH_2 concentration, hence the importance of reactions (6) and (8) over that of reaction (4). It appears, therefore, that the reactions involving NH_2 and/or species whose precursor is NH_2 might not be excluded as a source of hydrogen. One such example is seen in the reaction included by Dainton *et al.*[16] in the mechanism of radiolysis of liquid ammonia.

$$NH_2 + N_2H_3 \rightarrow NH_3 + N_2 + H_2 \qquad \Delta H = -99\ \text{kcal/mol} \qquad (9)$$

Addition of hydrazine to ammonia as the scavenger for hydrogen atoms would, at the same time, increase such possibilities even at ~20°C, while with propane as additive the main reaction paths are (1) and (2), which do not lead to such possibilities.

Explanation of $G_H=12.5$ analogous to what has been advanced to account for $G_H=11.7$ of water vapor in terms of the neutralization $H_3O^++e^-\rightarrow 2H+OH$[17] is not feasible, since if $NH_4^++e^-\rightarrow NH_2+2H$ occurs in ammonia at a higher tempera-

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[15] M. Schiavello and G. G. Volpi, *J. Chem. Phys.*, **37**, 1510 (1962).

[16] F. S. Dainton, T. Skwarski, D. Smithies and E. Wezranowski, *Trans. Faraday Soc.*, **60**, 1068 (1964).

[17] E. J. Hart and R. L. Platzman, "Mechanisms in Radiobiology," Vol. 1, Academic Press, New York (1961), p. 176.

ture where the extent of clustering would be less than that at 20°C, hydrogen yield from $NH_3+C_3H_8$ mixtures should increase in controversy to the observation. Futhermore, the reaction

$$NH_4^+\cdot(NH_3)_2 + e^- \rightarrow 2NH_3 + NH_2 + 2H$$

is endothermic by 40 kcal/mol[18] and $NH_4^+\cdot(NH_3)_2$ is the most abundant ions observed at 1 Torr and 100°C.[19]

Sulfur hexafluoride does seem to react with H atoms as well as electrons in the radiolysis of NH_3+SF_6 mixtures, as is indicated by the marked decrease in $G(H_2)$ which approaches the value obtained using olefins as additives, although the reaction of H atoms with SF_6 is reported to be slow.[20] It is not unreasonable, since the reaction $H+NH_3\rightarrow NH_2+H_2$ does not proceed at room temperature. Other possibilities such as quenching of precursor for H atoms by SF_6 cannot be ruled out.

The reactions of SF_6 and N_2O may be considered to be solely the scavenging of electrons in the $NH_3+C_3H_8$ system, since the molar ratio N_2O/C_3H_8 and SF_6/C_3H_8 in the present work are well below those reported by Johnson and Simic[9] where the reaction of H atoms with N_2O and with SF_6 can be excluded. The decrease in the yield of hydrogen by these additives may, therefore, be assumed to be due to the change in the neutralization process of ammonium ions from ion-electron to ion-ion. The depression of the hydrogen yield, $\Delta G(H_2)=3$—4, shown in Fig. 1 (the difference was taken from the uncorrected values of $G(H_2)$ as an approximation), is of the order of $100/W$ and is consistent with the change of the neutralization process from $NH_4^++e^-\rightarrow NH_2+H$, to the ion-ion recombination, where no hydrogen is produced. On the other hand, in Fig. 2, the plot of $G(H_2)_t$ with SF_6 and with N_2O vs. f_p both extrapolate to $G(H_2)^\circ=3.8$. The difference in $G(H_2)^\circ$ in the presence and absence of electron scavengers in this case is only ~ 2, which is significantly lower than the value estimated from W-value, if it really represents the contribution of ionic processes. The increase in the $\Delta G(H_2)$ with propane concentration in Fig. 2 may suggest that these electron scavengers influence hydrogen formation in the propane fraction more strongly. In ammonia+propane system all the ions are supposed to be rapidly converted into NH_4^+ by the ion-molecule reactions before neutralization.

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 \tag{10}$$

$$NH_2^+ + NH_3 \rightarrow NH_3^+ + NH_2 \tag{11}$$

$$RH^+ + NH_3 \rightarrow NH_4^+ + R \tag{12}$$

where RH^+ represents hydrocarbon ions. The dose rate employed in the present work might be in the region where electrons can diffuse to the wall and the neutralization at wall can compete with that in the gas phase. In fact, $\sim 5\times 10^{11}$ eV/$ml\cdot$sec of the present work lines in the range where Woodward and Back[21] observed the depression of hydrogen yield for a variety of hydrocarbons which was explained in terms of the stabilization of species formed by the wall neutralization. If the neutralization of NH_4^+ takes place at the wall, hydrogen is bound to be produced, although some stability was shown for the species NH_4.[12] The lower value of $G(H_2)^\circ$ estimated in Fig. 2 may be ascribed to the competition between neutralization of ammonium ions in the gas phase and at the wall. At the present stage, the experimental data are still by far insufficient to decide which of the $\Delta G(H_2)$ by electron scavengers is the true measure of the importance of ionic processes.

The slope of the straight line for $NH_3+C_3H_8+N_2O$ system gives $G(H_2)_p^\circ=4.5\pm 0.4$ in comparison to $G(H_2)=4.9$ of the propane radiolysis in the presence of N_2O determined by Johnson and Warman.[8] The slope of the line with SF_6 as electron scavenger and the difference from the line with N_2O are still puzzling. The effect of impurities in SF_6 may be ruled out, because the discrepancy becomes larger with propane concentration if SF_6 concentration is kept constant to that of ammonia. The trend may suggest the presence of some kind of interactions between SF_6 and propane. Another possibility is the production of hydrogen by the reaction of N_2O, for example, with NH_2. $G(N_2)=9.8$ at $N_2O/NH_3=0.05$ is markedly depressed by the addition of propane to $G(N_2)=3.5$ over the concentration range of 1 to 3 mol%, suggesting the principal mode of reaction between NH_2 and N_2O is to produce nitrogen, however, reactions such as

$$NH_2 + N_2O \rightarrow N_3 + H_2O$$

$$N_3 + NH_3 \rightarrow 2N_2 + H_2 + H$$

cannot be ruled out. In any case, the study using isotopically labeled additives together with the electron scavengers is definitely necessary to obtain informations for the elucidation of the discrepancy.

We should like to acknowledge valuable discussion with Dr. K. Fueki of Nagoya University and with Dr. N. Shinohara of Yokohama City University.

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[18] Thermochemical data used in the calculation are: Ionization potential; $NH_4=5.9$ eV,[12] $H=13.6$ eV; Proton affinity; $NH_3=202$ kcal/mol,[13] Heat of clustering of NH_4^+; $\Delta H_{0,2}=-46.3$ kcal/mol,[19] $D(H_2N\text{–}H)=104$ kcal/mol.

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[21] T. W. Woodward and R. A. Back, *Can. J. Chem.*, **41**, 1463 (1963).