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Effect of Additives in the Radiolysis of Gaseous Ammonia at High Densities

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The effect of additives and density on the radiolysis of ammonia at 140°C was studied over the density range 0.07 to 0.13 g/cc. The observation of a sharp decrease of G values in the radiolysis of pure ammonia at $d \sim 0.1$ g/cc confirmed the result reported by Toi *et al.* (*Radiation Res.*, **17**, 399 (1962)). The yield of hydrogen in the presence of ~ 1.5 mol% C_3H_6 was practically independent of density at $G=0.65$ over the density range studied. $G(H_2)$ in the presence of C_3H_8, estimated by extrapolation to zero propane concentration, was also constant at $G \simeq 5.7$ at $d \simeq 0.07$ and 0.13 g/cc. These observations were discussed in relation to the mechanism for depression of G values in the radiolysis of pure ammonia at higher densities.

The radiolysis of gaseous ammonia at high densities above the critical temperature has been investigated by Toi *et al.*[1] They observed a sharp depression in $G(H_2)$ and $G(N_2)$ at a density near 0.1 g/cc and concluded that such a decrease is consistent with the formation of ion clusters. Cluster formation in the irradiated ammonia has in fact observed in the high-pressure mass spectrometer,[2] apparently in support of their conclusion. However, the fact that observed ionic species are only clusters of $NH_4^+ \cdot (NH_3)_n$ type, with n as large as 20 at 200 Torr, implies that, if the ion clustering is to be invoked as the process responsible for the decrease, neutralization of charge in such a density region involves ion-ion recombination, since the neutralization of NH_4^+ whether clustered or unclustered is bound to end up in hydrogen formation as long as it occurs by way of ion-electron recombination. One such possibility as the mechanism at high densities has been proposed in a previous publication in terms of the neutralization between NH_4^+ and NH_2^-.[3] In an attempt to provide further informations as to the processes occuring at a high density, the effect of additives such as propylene and propane, which act as hydrogen atom scavengers, was investigated over the density range of 0.065 to 0.13 g/cc at 140±1°C.

Experimental

Purification of materials was described.[3] Gas chromatographic analysis of propane indicated that no organic impurities were present at levels exceeding 10^{-3} mol%.

Irradiations were carried out in glass cells of about 2 m*l* made of a glass tubing of 7 mm in outer diameter and 5 mm in inner diameter without a break-seal placed in a stainless steel autoclave in which a known volume of ammonia was introduced in order to balance the pressure in- and outside of glass cells. During irradiation in a source of approximately 1000 Ci of ^{60}Co, temperature was kept constant at 140±1°C by a heater with thermostat.

The absorbed dose in ammonia (E_a) was calculated from that determined by Fricke dosimetry on the basis

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[1] Y. Toi, D. B. Peterson and M. Burton, *Radiation Res.*, **17**, 399 (1962).

[2] A. M. Hogg and P. Kebarle, *J. Chem. Phys.*, **43**, 449 (1965).

[3] M. Nishikawa and N. Shinohara, *Radiation Res.*, **33**, 194 (1968).

of electron density ratios. It was previously shown by Toi *et al.*1) that the calculation is permissible in the density range $d \gtrsim 0.07$ g/cc. The dose absorbed in propane (E_p) was calculated from E_a using the ratio of stopping powers obtained by Meisels.4) The dose rate in ammonia at $d=0.10$ g/cc was 2.34×10^{13} eV/m*l*/sec.

The products non-condensable at 77°K were analyzed by combustion over cupric oxide in a furnace heated at $\gtrsim$350°C.

Results and Discussion

Figure 1 shows the dependence on density of the yield of hydrogen from pure ammonia, ammonia mixed with propylene, and with propane. The concentration of propylene (~1.5 mol%) was indicated to be sufficient as the H atom scavenger by a previous study.3) The yield of hydrogen in the presence of propylene is demonstrated to be practically independent of density at $G(H_2)=0.61$—0.69, which is in agreement with $G_{H_2}=0.74$ determined previously at 50 cmHg and 22°C,3) and also with $G(H_2)=0.70$ cited as a lower limit for G_{H_2} in liquid ammonia at 20°C.5),*1 The dependence of $G(H_2)$ on the propane concentration is essentially the same as that observed at the ammonia pressure ~50 cmHg and 22°C. Since hydrogen is one of the main products of propane radiolysis, correction is necessary for determining the yield of hydrogen from the ammonia fraction *via* the reaction

$$H + C_3H_8 \rightarrow H_2 + C_3H_7 \qquad (1)$$

and *via* the processes leading to molecular hydrogen. The estimate of the contribution of propane fraction to hydrogen production was made by plotting *G*-values of the total hydrogen ($G(H_2)_t$) calculated for the total energy absorbed by the mixture ($E_t=E_a+E_p$) against the fraction of energy absorbed by propane ($f_p=E_p/E_t$). The plot is based on the equation which is applicable only in the region where energy transfer between the components of the mixture is negligible;

$$G(H_2)_t = G(H_2)^\circ_a \cdot f_a + G(H_2)^\circ_p \cdot f_p$$

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 deposited, *i. e.*, $f_a+f_p=1$. Figure 2 shows that $G(H_2)_t$ at high densities lies, within the experimental error, on the same straight line obtained at ~50 cmHg and 22°C. Extrapolation to $f_p=0$, by the least square method over the points including those for ~50 cmHg, yields $G(H_2)^\circ_a=5.74\pm0.13$, which should be a measure of $G_H+G_{H_2}$ of ammonia radiolysis. $G_H=5.1$ thus determined is significantly lower than the values hitherto reported.7),8) The disagreement in the value of G_H will be discussed elsewhere.6)

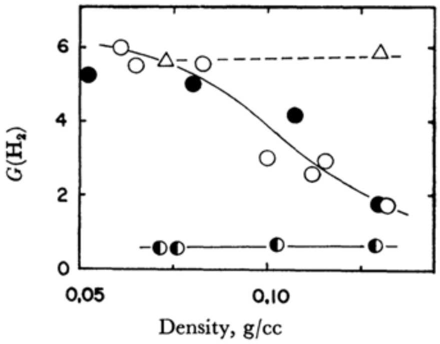

Fig. 1. Effect of density on $G(H_2)$ in the radiolysis of ammonia at 140°C.
○, from pure ammonia (this work); ●, (Toi *et al.*1)); △, with propane (the intercept of Fig. 2); ◐, with propylene.

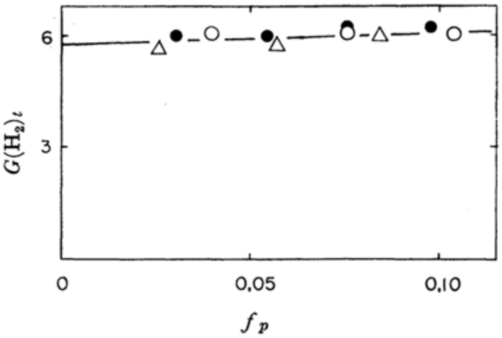

Fig. 2. Dependence of $G(H_2)_t$ from $NH_3 + C_3H_8$ mixtures at 140°C on the fraction of energy absorbed by C_3H_8 ($f_p = E_p/E_t$).
○, $d \cong 0.13$ g/cc; △, $d \cong 0.07$ g/cc;
●, $d \cong 0.0005$g/cc (~50 cmHg) at 22°C

The observed yield of hydrogen in the presence of propylene and of propane appears to indicate that G_H and G_{H_2} are independent of temperature and density. "Molecular" hydrogen seems less likely to be associated with the observed depression in the yield at $d \cong 0.1$ g/cc as it is relatively unimportant at the lower density region. It is, therefore, the behavior of G_H that is playing the major role in the observed phenomenon. The finding that G_H is apparently constant at $d \cong 0.07$ and at 0.13 g/cc

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4) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

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

*1 The value is also in agreement with $G(H_2)=0.81$ at $d=0.15$ g/cc and 17°C determined using 1.5 mol% C_2D_4. (M. Nishikawa, D. B. Peterson and M. Burton, unpublished.)

6) To be published separately.

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

8) G. R. A. Johnson and M. Simic, *Nature*, **216**, 479 (1967).

may be interpreted at least in two ways in this regard. First the yield of hydrogen atoms is really independent of density; it follows that the processes responsible for the depression must be those in which hydrogen atoms disappear with the precursor for nitrogen. Secondly the apparent constancy of G_H is due to alterations in the reaction paths caused by the addition of propane, and that in pure ammonia G_H itself is influenced by the density change. For the former case, one of the most probable processes is the geminate recombination of radical pairs

$$H + NH_2 \xrightarrow{M} NH_3 \qquad (2)$$

whose specific rate is estimated to be 1.2×10^{10} M$^{-1}\cdot$sec^{-1} at 1 atm.[9] This reaction appears to be favored by higher density because of the track effect leading to relatively high local concentration of radicals. However, Toi *et al.* noted that the track effect is not sufficiently sensitive to density to account for the sudden decrease in the yield. Furthermore, the specific rate for the reaction

$$H + NH_3 \longrightarrow NH_2 + H_2 \qquad (3)$$

is of the order of 10^4 M$^{-1}\cdot$sec^{-1} at 140°C,[10] so that it is expected to compete successfully with (2) in the bulk ammonia. The extent of "cage" effect $d \sim 0.1$ g/cc and 140°C would not be large enough for reaction (2) to be efficient. Then, the latter seems to be more likely.

$G(N_2)$ in the presence of 1—3 mol% propane is 0.6 at $d=0.07$ and 0.13 g/cc, which is markedly lower than $G(N_2)=1.7$ in the pure ammonia at $d=0.07$ g/cc, but about equal at $d=0.13$ g/cc. The depression of $G(N_2)$ by propane suggests the occurrence of the reaction

$$NH_2 + C_3H_8 \longrightarrow NH_3 + C_3H_7 \qquad (4)$$

If reaction (4) proceeds faster at 140°C than the reaction

$$NH_2 + e^- \longrightarrow NH_2^- \qquad (5)$$

which was included in the mechanism proposed to explain the depression of G values in pure ammonia at $d \sim 0.1$ g/cc, the apparent independence of $G(H_2)$ on density observed in the $NH_3+C_3H_8$ mixtures is compatible with the mechanism; namely, in pure ammonia at high densities, the presence of large clusters lowers the electrostatic field of NH_4^+ to such an extent that reaction (5) can compete for electrons, and the neutralization NH_4^+(clustered) + NH_2^-(clustered)$\rightarrow 2NH_3$ reduces both $G(H_2)$ and $G(N_2)$, while in the presence of propane the neutralization $NH_4^+ + e^- \rightarrow H + NH_3$ takes place, which followed by reaction (1) keeps the yield of hydrogen constant. The difference in $G(H_2)$ of pure ammonia at $d=0.07$ and at 0.13 g/cc, $\Delta G(H_2) \simeq 4.5$, is somewhat larger than the value of $100/W$ ($W=26.5$ eV[4]), which is expected if it is to be related to the change in the neutralization process. This apparently excessive decrease might also be explained by the depletion of NH_2 *via* reaction (5) which inhibits processes leading to additional hydrogen formation from precursors other than H atoms. The observation that at 1 atm $G(H_2)$ from pure ammonia at $\gtrsim$100°C is significantly larger than $G(H_2)$ in the presence of propane at the same temperature[8] suggests the occurrence of such processes as a mode of hydrogen formation at a higher temperature, since all the H atoms are expected to be converted into H_2 by reaction (1) in the presence of propane, and by reaction (3) in pure ammonia. This mechanism has the desired sensitivity to density, since it is based on the presence of large clusters. The observation that N_2O has little effect on $G(H_2)$ in liquid ammonia[5] appears to support the mechanism in which it suggests the neutralization in the liquid phase is occurring mostly by $NH_4^+ + NH_2^-$. It is desirable to test the effect of electron scavengers in this density range to see if there is change in the importance of ionic processes. However, most of the compounds used for such a purpose act as hydrogen atom scavenger as well at 140°C, and since the addition of propane has the possibility of changing the reaction paths, neither the use of electron scavengers together with propane can be expected to yield useful informations in this regard. At this stage,the present study could not confirm the proposed mechanism, but appears, at least, to be consistent with it.

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9) M. H. Hanes and E. J. Blair, *J. Chem. Phys.*, **38**, 672 (1963).

10) M. Schiavello and G. G. Volpi, *ibid.*, **37**, 1510 (1962).