Effect of Hydrogen Atom and Electron Scavengers on the Gas-Phase Radiolysis of Ammonia

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Toi *et al.* proposed the ion clustering as the process responsible for the sudden decrease in $G(-NH_3)$ in the radiolysis of ammonia at higher densities, where it is implied that 57—76% of the total decomposition in the low density region is due to processes involving ions.[1]

We wish to report some of the results of our experiment where the effect of various additives to the radiolysis of ammonia at ~50 cmHg at 20°C was studied.

Glass vessels of *ca.* 50 m*l* fitted with break-off seal were used as the irradiation cell in a ~1000C ^{60}Co source. Gases of rated purity above 99.5% were used after distillation. Dosimetry was carried out by measuring nitrogen and oxygen produced in the radiolysis of nitrous oxide at ~60 cmHg by taking $G(N_2+O_2)=12.0$.[2] The dose rate in ammonia was calculated on the basis of electron density ratios. The gaseous products, nitrogen and hydrogen, were collected in a Saunders-Taylor apparatus and hydrogen was separated from nitrogen by passing over heated cupric oxide.

We found that $G(H_2)$ fell from 4.3 to 2.5 at N_2O concentrations greater than 5 mol%; $G(H_2)$ is 0.64 in the presence of CCl_4 above 2 mol%, while in the presence of C_2H_4 or C_3H_6 over the concentration range 1.5—3.8 mol% it is between 0.70 and 0.82. The gas chromatogram of gaseous products from NH_3+CCl_4 before condensation of the irradiated mixture at 77°K showed the presence of a peak which was assigned to HCl. At the same time a white solid substance was observed to be deposited on the wall of irradiation cells, which was identified to be NH_4Cl by the qualitative and the quantitative analysis for NH_4^+ and Cl^-. These observations suggest that CCl_4 is acting both as the H atom and as the electron scavengers in ammonia by the reactions such as:

$$CCl_4 + e^- \rightarrow CCl_3 + Cl^- \quad (1)$$

$$NH_4^+ + Cl^- \rightarrow NH_4Cl \quad (2)^{3)}$$

$$CCl_4 + H \rightarrow CCl_3 + HCl \quad \Delta H = -34 \text{ kcal/mol}^{4)} \quad (3)$$

1) Y. Toi, D. B. Peterson and M. Burton, *Radiation Res.*, **17**, 399 (1962).
2) F. T. Jones and T. J. Sworski, *J. Phys. Chem.*, **70**, 1546 (1966).
3) The ionic species present in irradiated ammonia at near-atmospheric pressure are shown to be composed of NH_4^+ and its clusters of various sizes. See A. M. Hogg and P. Kebarle, *J. Chem. Phys.*, **43**, 449 (1965).
4) S. C. Lind, "Radiation Chemistry of Gases, Appendix," Reinhold, New York (1961).

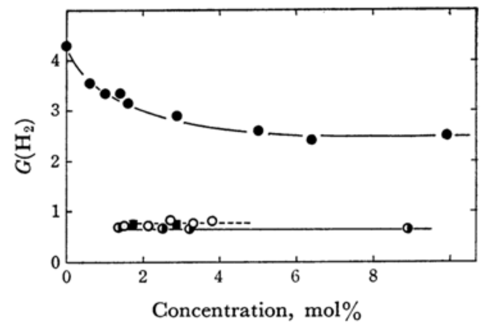

Fig. 1. Effect of H atom and electron scavengers upon $G(H_2)$ from the radiolysis of ammonia.
●, N_2O; ○, C_3H_6; ■, C_2H_4; ◑, CCl_4

The change in $G(H_2)$ by N_2O, $\Delta G(H_2)=1.8$, may be attributed to the change in the neutralization process of NH_4^+ from (4) and (5) to that involving ion-ion recombination. If it is assumed that ion-ion recombination of NH_4^+ such as (7)

$$NH_4^+ + e^- \rightarrow H \quad (4)$$

$$\rightarrow H_2 \quad (5)$$

$$N_2O + e^- \rightarrow N_2 + O^- \quad (6)$$

$$NH_4^+ + O^- \text{ or } O_2^- \rightarrow \text{no H, } H_2 \quad (7)$$

does not produce hydrogen, the ratio of $\Delta G(H_2)$ by N_2O to $G(H_2)$, 0.42, should represent the contribution from processes involving ions to the hydrogen production from the radiolysis of ammonia at 20°C near the atmospheric pressure. Since the olefins used are expected to behave exclusively as the H atom scavenger,[5] the difference in the yield of unscavengeable hydrogen from olefin-NH_3 and from CCl_4-NH_3 mixtures may be attributed to reaction(5), *i. e.* 0.06—0.16 in $G(H_2)$, which contributes to only 3—9% of hydrogen via ionic processes. The observation by Miyazaki and Shida that hydrogen yield from the radiolysis of *n*-butane-ammonia-pentene mixture gradually increases with ammonia concentration[6] is in agreement with the present finding, which may also corroborate the validity of the assumption to ignore (5), involved in the use of ammonia as the proton acceptor in the radiolysis of hydrocarbons.[7]

5) Thermochemical data predict charge, proton-, and H_2-transfer from NH_4^+ to the olefins are unlikely.
6) T. Miyazaki and S. Shida, This Bulletin, **38**, 2114 (1965).
7) Ff. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).