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

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Recently, two different values were reported for the yield of hydrogen atoms in the radiolysis of ammonia vapor ; $G_H = 12.5 \pm 1$ by Jones and Sworski from their study on $NH_3 + D_2$ and $NH_3 + N_2H_4$ system,[1] and $G_H \gtrsim 7.2$ by Johnson and Simic on $NH_3 + C_3H_8$ system.[2] In this communication, we wish to report some of the results of our study on the γ-radiolysis of $NH_3 + C_3H_8$ system which indicate still lower G_H from ammonia.

Purification of ammonia (99.9%, Matheson) and propane (>99.8%) and the method of irradiation were described.[3] Gas chromatographic analysis of propane indicated that no organic impurities were present at levels exceeding 10^{-3} mol%. The amount of energy absorbed in ammonia fraction (E_a) and in propane fraction (E_p) were calculated from that in a nitrous oxide dosimeter, assuming $G(N_2) = 10.0$,[4] for the runs at near-atmospheric pressure, and a Fricke dosimeter at higher densities, using the relative stopping powers obtained by Meisels.[5] The non-condensable products H_2 and N_2 were analyzed by combustion in a cupric oxide furnace.

The total hydrogen yield calculated for energy absorbed in ammonia fraction increased from $G(H_2) = 4.1$ to 7.8 at the propane concentration of 8.6 mol% in agreement with Johnson's value.[2] However, in contrast to their observation, no plateau was reached up to this concentration, suggesting hydrogen formation from the direct radiolysis of propane fraction. Therefore, in order to estimate the contribution of propane fraction for the observed yield of hydrogen, G-values of total hydrogen yields (G_t) were calculated for the total energy absorbed by the system ($E_t = E_a + E_p$) and are plotted against the fraction of energy absorbed in propane ($f_p = E_p/E_t$) in Fig. 1. A good straight-line relationship is demonstrated for f_p below 0.13 regardless of density and/or temperature and extrapolation to $f_p = 0$ yields $G(H_2)^\circ = 5.84$.

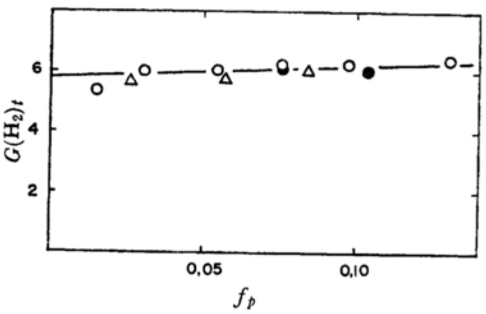

Fig. 1. Dependence of $G(H_2)_t$ on the fraction of energy absorbed by C_3H_8.
○, d~5.0×10^{-4} g/cc, 22°C
△, d~0.065 g/cc, 140°C
●, d~0.13 g/cc, 140°C

Hydrogen atoms react with propane by $H + C_3H_8 \rightarrow H_2 + C_3H_7$. The yield of hydrogen at $f_p = 0$, $G(H_2)^\circ = 5.84$, is therefore a measure of the total yield of hydrogen atoms and the molecular hydrogen from the radiolysis of ammonia vapor. The latter has been determined to be 0.74,[3] hence $G_H = 5.84 - 0.74 = 5.10$.

The value of G_H thus obtained is significantly lower than those reported by Jones and Sworski[1] and by Johnson and Simic.[2] The disagreement with Johnson's value may be probably due to their neglect of hydrogen produced from propane radiolysis. It seems inconceivable in view of the large value of the relative stopping power of propane, $s_p/s_a = 2.65$,[5] that no hydrogen is produced from propane, for example, at 6 mol% where they observed the plateau in $G(H_2)$. The more serious disagreement with Sworski's value might be inherent in the system they used. For $NH_3 + D_2$ system, they also noted that G_H as high as 90 ± 66 was obtained from their proposed mechanism at the total pressure of 600 mmHg, suggesting some kind of chain mechanism is operating. For $NH_3 + N_2H_4$ system, their mechanism does not include reactions such as $NH_2 + N_2H_3 \rightarrow NH_3 + N_2 + H_2$ ($\Delta H = -99$ kcal/mol) proposed by Dainton *et al.*,[6] the inclusion of which should lower the estimate of G_H. The use of $NH_3 + C_3H_8$ system with proper corrections for hydrogen produced from propane appears more straight-forward and less ambiguous for the estimate of G_H from ammonia radiolysis.

1) F. T. Jones and T. J. Sworski, *Trans. Faraday Soc.*, **63**, 2411 (1967).
2) G. R. A. Johnson and M. Simic, *Nature*, **216**, 479 (1967).
3) M. Nishikawa and N. Shinohara, *Radiation Res.*, **33**, 194 (1968).
4) F. T. Jones and T. J. Sworski, *J. Phys. Chem.*, **70**, 1546 (1966).
5) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).
6) F. S. Dainton, T. Skwarski, D. Smithies and E. Wezranowski, *Trans. Faraday Soc.*, **60**, 1068 (1964).