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Radiolysis of Ammonia

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The radiolysis of ammonia has been studied extensively, the primary process of hydrogen formation in particular, being investigated in detail. The results have led to the conclusion that the G values of non-scavengeable hydrogen molecules are 0.64—0.84 and those of thermal (scavengeable) hydrogen radicals 5—12.[1–7]

We studied the formation of hydrogen from mixtures of ammonia and olefins (ethylene, propylene and butadiene).[1] From kinetic calculation, we concluded that non-scavengeable hydrogen molecules produced by the radiolysis of ammonia are mainly produced by a unimolecular process. The bimolecular process is less important, *i.e.*, $k_{bi}/k_{uni}<0.36$, $k_{bi}\approx 0$.

In this paper we report on the result of radiolysis of a gaseous mixture of ammonia and perdeuterated ammonia. Consideration is given to the precise determination of the ratio of the rate constant (k_{uni}/k_{bi}).

Ammonia and nitrous oxide were purified by the same method as described previously.[1] Perdeuterated ammonia (Merk, Sharp and Dohm Ltd., isotopic purity 98 at % D) was purified by the same method as that for ammonia.

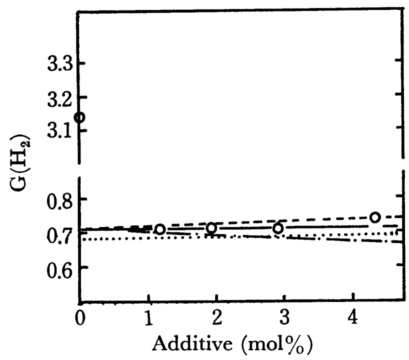

Fig. 1. Effects of scavengers on hydrogen formation
-○-: NO, ⋯⋯: C_2H_4, ----: C_3H_6, -·-·-: C_4H_6

Results and Discussion

Figure 1 shows the effect of scavenger (NO) on hydrogen formation together with the previous results of the addition of olefin (ethylene, propylene and butadiene).[1] No effects such as seen in the system of ammonia and olefins are observed by the addition of NO. The limiting value of $G(H_2)$ is 0.72 which is in good agreement with the values of non-scavengeable hydrogen molecules.

A non-scavengeable hydrogen molecule probably arises for the most part form the decomposition of the superexcited ammonia molecule (NH_3^{**}) *via* the reaction[1]

$$ND_3^{**} \xrightarrow{k_{uni}} ND + D_2 \qquad (1)$$

An alternative explanation is that some hot hydrogen radicals (H) are formed and they may abstract hydrogen from ammonia:

$$ND_3^{**} \xrightarrow{k_{bi}} ND_2 + D \qquad (2)$$

By a simple kinetic treatment, we can derive the following equation.

$$\lim_{[ND_3]\to 0} D_2/HD = \frac{k_{uni}}{2k_{bi}} \qquad (3)$$

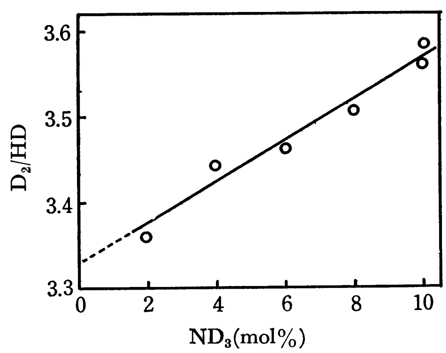

Fig. 2. D_2/HD *vs.* concentration of ND_3

Figure 2 shows the relationship between the concentration of perdeuterated ammonia and D_2/HD in the radiolysis of NH_3–ND_3–NO(NO=7%). A good straight line is given and from its intercept the following value is obtained.

$$k_{uni}/2k_{bi} = 3.33$$

The results lead to the conclusion that about 87% of non-scavengeable hydrogen molecules produced by the radiolysis of ammonia are produced by reaction (1), or by a unimolecular process.

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