Hydrogen Formation in the Radiolysis of Ethylamine

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Summary The yield of hydrogen on radiolysis of pure ethylamine at room temperature is $5\cdot5 \pm 0\cdot1$ and has three precursors: electrons ($G = 2\cdot1 \pm 0\cdot1$), hydrogen atoms ($G \simeq 0\cdot7$), and unscavengeable hydrogen ($G \leqslant 2\cdot7$); the maximum yield of scavengeable electrons is 2·7.

SAMPLES of anhydrous ethylamine (from B.D.H.) (degassed and distilled over NaOH pellets into the irradiation ampoules) were irradiated with ^{60}Co γ-radiation at a dose rate of 6×10^{17} ev/g×min, with doses up to 7×10^{18} ev/g; (samples containing SF_6 were irradiated with doses up to 5×10^{19} ev/g in order to determine the fluoride concentration).

Hydrogen and nitrogen were determined by g.l.c. and fluoride ion by titration with $Th(NO_3)_4$.[1] The concentrations of gaseous scavengers in solutions were determined using the Ostwald distribution coefficients α (equal to $2\cdot9 \pm 0\cdot2$, $2\cdot3 \pm 0\cdot2$, and $1\cdot1 \pm 0\cdot8$ for nitrous oxide, ethylene, and sulphur hexafluoride, respectively) estimated as described elsewhere.[2]

The yields of all products are dose-independent. The yield of hydrogen in pure ethylamine is $5\cdot5 \pm 0\cdot1$. In the presence of SF_6 and N_2O at concentrations of *ca.* 1×10^{-2} M and *ca.* 2×10^{-2} M the yield of hydrogen drops to 3·3 and 3·5, respectively (Figure 1). We can regard the suppression of hydrogen yield as the scavenging of solvated electrons—precursors of hydrogen—with a yield $G = 2\cdot1 \pm 0\cdot1$.

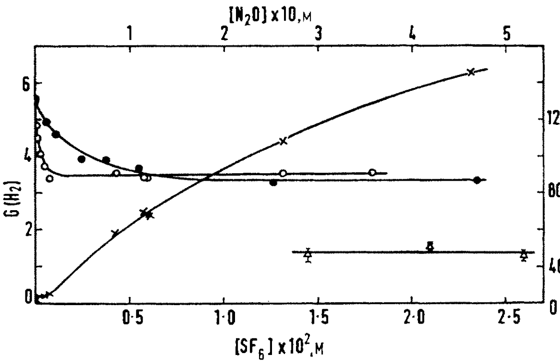

FIGURE 1. *Variation of* $G(H_2)$ (○) *and* $G(N_2)$ (×) *with* $[N_2O]$ *and of* $G(H)_2$ (●) *and* $G(F^-)$ (△) *with* $[SF_6]$.

Rigorously, simple competition kinetics, $\{\Delta G(H_2)\}^{-1}$ against $[S]^{-1}$, for evaluation of the yield of electrons and the ratio of reaction rates cannot be used in this case. The dielectric constant of ethylamine[3] is 6·17 and the yield of electrons ("free ions") should be, according to Freeman,[4] about 0·3—0·4. From the determined value of 2·1 one can see that the electrons in spurs are scavenged, and hence inhomogeneous kinetics should be applied. Nevertheless, Figure 2 shows that the homogeneous competition kinetic relationship is in satisfactory agreement with the experimental data in the concentration range used. The rate constant for the reaction of electrons with ethylamine calculated from the data in Figure 2 using $k(e^-_{aq} + N_2O) = 5\cdot6 \times 10^9$ M^{-1} s^{-1}[5] and $k(e^-_{aq} + SF_6) = 1\cdot65 \times 10^{10}$ M^{-1} s^{-1}[6] is 0·9 to 2×10^6 M^{-1} s^{-1}; the value of 9×10^5 M^{-1} s^{-1} was found for this reaction in aqueous solution.[7] This finding may possibly reflect a situation where a substantial proportion of electrons in a medium of low dielectric constant is distributed at distances of a few nanometres around the geminate cations at times when scavenging may occur; the distances between scavenger molecules are of the same order, which may allow the scavenging of electrons to approximate to homogeneous kinetics.

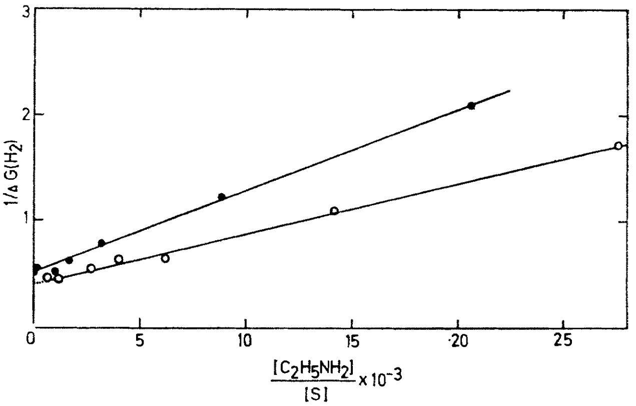

FIGURE 2. *Competition for* e^-_s *between ethylamine and* N_2O (●) *or* SF_6 (○).

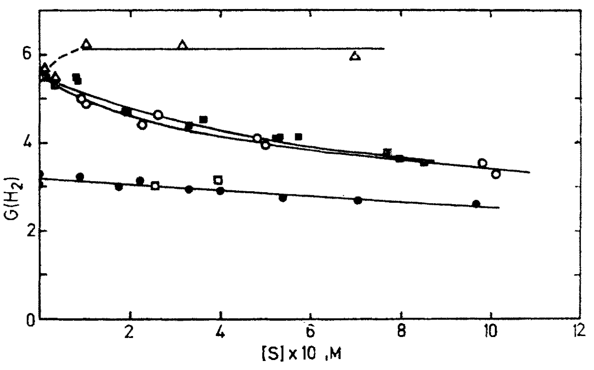

FIGURE 3. *Variation of* $G(H_2)$ *with the concentration of ethylamine hydrochloride* (△), *ethylene* (■), *allyl alcohol* (○); *variation of* $G(H_2)$ *with the concentration of ethylene* (□) *or allyl alcohol* (●) *in the presence of* ca. 0·1 M-N_2O.

The formation of some of the hydrogen by mechanisms other than reactions of electrons can be distinguished in experiments where electrons yielding hydrogen are scavenged by N_2O, and a further decrease in hydrogen formation is effected by increasing the concentration of allyl alcohol (Figure 3). The maximum decrease of the hydrogen yield (*ca.* 0·7) at 1M allyl alcohol concentration can be interpreted as scavenging of hydrogen atoms formed independently of reactions of electrons. The effect of high concentrations of solutes is of course complex, and such solutions should be treated as binary mixtures.

Ethylene or allyl alcohol, present alone, suppresses the hydrogen yield without achieving any distinct plateau and the scavenging efficiencies of the two compounds are nearly the same (Figure 3). The scavenging mechanism for these two compounds is not straightforward, as according to the values of the rate constants[5,8,9] they may scavenge both hydrogen atoms and electrons. Since the rate constants for addition of hydrogen atoms to ethylene and allyl alcohol are somewhat different ($5 \cdot 5 \times 10^{8}$ [8] and $2 \cdot 3 \times 10^{9}$ $\text{M}^{-1}\,\text{s}^{-1}$,[5] respectively) it is necessary to assume that reacting hydrogen atoms have an excess of energy, so that the difference in the reactivities of the compounds almost vanishes; the rate constant for hydrogen abstraction from ethylamine would be of the order of $10^{7}\ \text{M}^{-1}\,\text{s}^{-1}$. Considering the scavenging of electrons and using the value of $5 \times 10^{7}\ \text{M}^{-1}\,\text{s}^{-1}$ [9] (determined in methanol) for the rate constant of the reaction of electrons with allyl alcohol, then the rate constant for the reaction of electrons with ethylamine would be of the order of $10^{6}\ \text{M}^{-1}\,\text{s}^{-1}$ (*cf.* the values above).

The lowest yield of hydrogen observed can be considered as the unscavengeable value, irrespective of the mechanism of its formation; its value is $G(\text{H}_2, \text{unsc.}) \leqslant 2 \cdot 7$.

Ethylamine hydrochloride at a concentration $\geqslant 0 \cdot 1$ M enhances the yield of hydrogen by about 0·6 (Figure 3). This value can be attributed to the yield of electrons which react in pure ethylamine without forming hydrogen and which are scavenged by acid, producing hydrogen. The total yield of scavengeable electrons is then $G(\text{e}^{-}, \text{sc.}) = 2 \cdot 7$.

The yield of fluoride ions formed in the presence of SF_6 is 27 ± 4. If, as in aqueous solutions, each scavenged electron finally gave six fluoride ions,[6] a maximum yield of 16·2 would be expected. The difference of about 11 from the measured yield may be caused by a reaction of some radicals with SF_6.

The high yields of nitrogen in the presence of N_2O (Figure 1) indicate a chain reaction where electrons and reactive radicals may be chain carriers; in the simultaneous presence of N_2O and ethylene or allyl alcohol, which can scavenge both electrons and radicals, the yield of nitrogen is substantially decreased. The yield of nitrogen in pure ethylamine is $< 0 \cdot 1$.

The yield of hydrogen in ethylamine irradiated as a supercooled liquid at 193 K is 2·8, while in a polycrystalline sample irradiated at the same temperature it is 4·0; the yield in a polycrystalline sample irradiated at 77 K is 3·3. Similarly, in methanol irradiated at 169 K the yields of hydrogen were 3·4 and 3·9 for supercooled liquid and crystalline sample, respectively.[10] Thus the effect of the physical state is significant in the radiolysis of both compounds.

The results described here may be compared with the results of Smithies and Whitworth for liquid methylamine.[11]

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