Water Formation in the Gas Phase Radiolysis of Nitrous Oxide-Hydrocarbon Mixtures

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The determination of water formation in the radiolysis of nitrous oxide - hydrocarbon systems is important for the elucidation of radiolytic mechanism of pure nitrous oxide, as well as the electron-scavenging process of nitrous oxide in hydrocarbons.[1] However, information is scanty and inaccurate. In previous papers,[2] an ionic mechanism in the gas-phase radiolysis of nitrous oxide was proposed and the importance of processes other than the ionic process was suggested. In the present study, the effect of hydrocarbons on the gas-phase radiolysis of nitrous oxide has been examined.

A sample containing about 90 cmHg of N_2O with small amounts of the hydrocarbons, C_2H_6, C_3H_8, C_2H_4, or C_3H_6, was irradiated by ^{60}Co-γ rays at room temperature to a total dose of 2.1×10^{20} eV/g. The products were analyzed by gaschromatography using a molecular sieve-5A column at 60°C for N_2 and CO and a polyethyleneglycol-200 column at 70°C for other oxygen-containing products. Special care was taken in the analysis of the main product H_2O.

The addition of small amounts of hydrocarbons to N_2O caused a sudden decrease in the nitrogen yield and a large increase in the yield of oxygen-containing products, giving respective plateau values. In all cases, H_2O is the major product with small amounts of alcohols or CO. A typical result for C_2H_6 is given in Fig. 1. Decrease of the observed nitrogen yield was 2.5 in G unit for C_2H_6 and C_3H_8, 2.6 for C_2H_4, and 2.7 for C_3H_6. The total yields of oxygen-containing products were 6.8 for C_2H_6, 6.9 for C_3H_8, 6.8 for C_2H_4 and 6.4 for C_3H_6. They are roughly three times, as much as the decrements of the nitrogen yield. In the presence of the hydrocarbons, NO and O_2 were not detected.

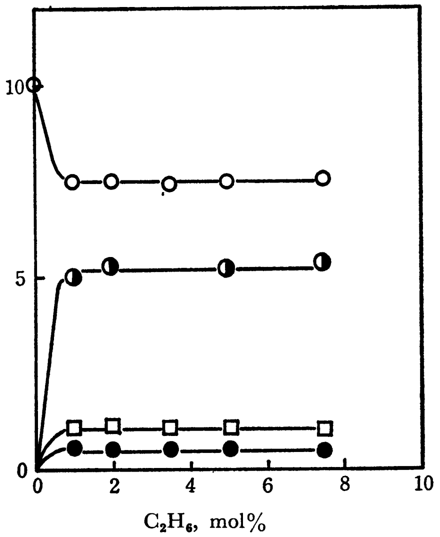

Fig. 1. The effect of C_2H_6 addition to N_2O.
○ N_2, ◑ H_2O, □ *i*-C_4H_9OH, ● C_2H_5OH.

From the results, the contribution from ionic processes is considered, for which the following schemes are assumed;[3]

$$N_2O \rightsquigarrow N_2O^+ + e^-,\quad N_2O^+ + RH \rightarrow N_2O + RH^+,$$
$$N_2O + e^- \rightarrow N_2O^-,$$
$$N_2O^- + RH\ (\text{or } RH^+) \rightarrow N_2 + OH^-\ (\text{or } OH) + R,$$
$$OH^- + RH^+ \rightarrow H_2O + R,\ \text{or}$$
$$OH^- + N_2O^+ \rightarrow N_2O + OH,\quad OH + RH \rightarrow H_2O + R.$$

According to these schemes, however, nitrogen should be produced as much as H_2O and the nitrogen yield should not decrease by the addition of a hydrocarbon. The observed decrease of the nitrogen yield, then, must be ascribed to some other processes. The total yield of the oxygen-containing products is much larger than the decrease of the nitrogen yield. It seems reasonable to assume the following non-ionic processes involving two kinds of oxygen atoms; one can contribute to the decomposition of N_2O but not the other,[4] both reacting with hydrocarbons to form oxygen-containing products.

$$N_2O \begin{array}{l} \rightsquigarrow N_2 + O, \quad O + N_2O \not\rightarrow \\ \rightsquigarrow N_2 + O^*, \quad O^* + N_2O \rightarrow N_2 + O_2,\ 2NO. \end{array}$$

On the basis of the observed decrements of the nitrogen yields in the presence of hydrocarbons, combined with the total G(NO) value and that contributed from ionic processes obtained in the radiolysis of pure N_2O,[2] it can be concluded that O* plays a major role in the non-ionic decomposition of N_2O. From the consideration of photochemical studies[5] on the reactivities of oxygen atoms, it may be inferred that O and O* are the ground $O(^3P)$ and the excited $O(^1D)$ or $O(^1S)$ atoms, respectively.

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