The Measurement of Water and Other Oxygen-containing Products in the Radiolysis of Cyclohexane Solutions of Nitrous Oxide

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Nitrous oxide has received more attention than any other solute among electron scavengers, but there is still considerable uncertainty as to the over-all mechanism of N_2 formation despite the large number of studies.[1] The difficulty in interpreting the results arises from the facts that the observed yield of N_2 is considerably greater than the expected yield of electron and that no quantitative analysis of all the oxygen-containing products formed after the decomposition of N_2O has yet been accomplished. As the oxygen-containing products, thus far, $C_6H_{11}OH$[2-4] and H_2O[5] have been reported to be formed in the cyclohexane-N_2O system.[6] The yield of $C_6H_{11}OH$, which accounted for only a small percentage of the expected yield of oxygen-containing products, was measured quantitatively. The previous measurements of H_2O, however, were quite inaccurate.[5,7,8] In the present study, the measurement of H_2O and other oxygen-containing products in the radiolysis of cyclohexane solutions of N_2O has been accurately carried out.

Cyclohexane was completely dehydrated before irradiation by using a liquid Na–K alloy. The samples, 2-m*l* portions of the cyclohexane with various N_2O concentrations, were irradiated by ^{60}Co-γ rays to a total dose of 9.2×10^{19}eV/g at room temperature. The total yields of H_2O and alcohols, denoted by ROH, were calculated stoichiometrically on the basis of H_2 yield produced by the reaction with the Na–K alloy after the removal of N_2O and radiolytic products of H_2 and N_2. The alloy, rather than either sodium or potassium alone, is preferable because the liquid alloy maintains a fresh active surface. The complete evolution of H_2 can be accomplished only if the alloy is free from its oxide, since the oxide reacts with H_2O without the liberation of H_2. The alloy was, therefore, carefully prepared in order to avoid the oxide. The accuracy of the method used for determining the total amounts of ROH was tested with several authentic samples in which a known amount of H_2O or $C_6H_{11}OH$ has been added to the completely dehydrated cyclohexane. The amount of H_2O or $C_6H_{11}OH$ added to the cyclohexane almost agreed with that computed from the yield of H_2. Especially great caution was used in the analysis of ROH containing the main product, H_2O, since the quantitative analysis of H_2O is known to be very difficult. In this experiment, good reproducibility and accuracy have been attained.[9] Furthermore, H_2O was not detected in the dehydrated cyclohexane either before or after irradiation. Oxygen-containing products other than H_2O were analyzed gas-chromatographically on a polyethyleneglycol-600 column at 100°C.

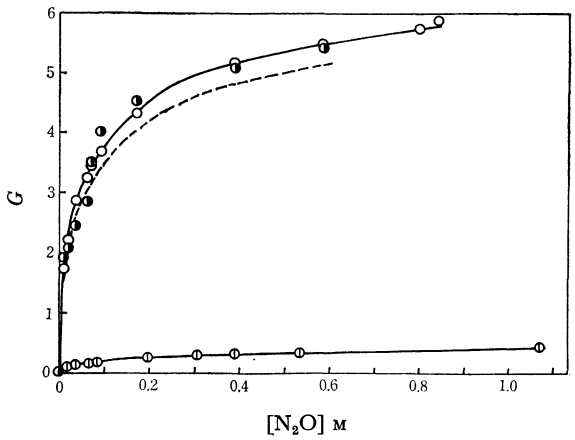

Fig. 1 Yields of N_2 (○), ROH (◑), $C_6H_{11}OH$ (⏀) and H_2O (---) from the cyclohexane-N_2O system.
The yield of H_2O is estimated by the difference between the yield of ROH and that of $C_6H_{11}OH$.

The yields of H_2 and N_2 at various N_2O concentrations approximately agree with those reported in earlier papars.[1] The yields of total ROH, $C_6H_{11}OH$ and H_2O obtained by the above method are shown in Figure 1. The yield of $C_6H_{11}OH$ approximately agrees with that previously reported.[3] The yield of total ROH surprisingly agrees with the yield of N_2 at all concentrations of N_2O. Figure 1 also shows that ROH consists of H_2O plus a small quantity of $C_6H_{11}OH$. No other oxygen-containing products, such as O_2, NO, aldehydes, ketones and ethers, were detected.

The above facts show that the decomposition of N_2O leads finally to the formation of N_2 and ROH in the ratio of one to one; this finding seems to be helpful in understanding the decomposition mechanism of N_2O in hydrocarbon solutions. Further study is now in progress.

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9) Very recently in our laboratory the quantitative analysis of H_2O in the gas-phase radiolysis of N_2O-hydrocarbon mixtures has also been carried out gas-chromatographically.[10]
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