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The Decomposition of Nitrous Oxide in the Radiolysis of *n*-Hexane Solutions

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Synopsis. The effect of the addition of N_2O (10^{-2}—10^{-4} mole fraction) in the radiolysis of liquid *n*-hexane has been examined. The oxygen-containing products such as water and alcohols have been detected. The number of nitrogen molecules produced per an electron scavenged by N_2O exceeds unity even at the lowest concentration.

Nitrous oxide has been widely used as an electron scavenger in radiation chemistry. The mechanism of its decomposition when dissolved in saturated hydrocarbons, however, is not yet fully understood.3,4)

In this work, the γ-radiolysis of liquid *n*-hexane containing N_2O has been carried out in order to establish the quantitative relationship between the nitrogen yield and the decrease in the hydrogen yield as well as the stoichiometry4) of the decomposition of N_2O.

Experimental

The *n*-hexane was a Phillips research-grade material. The gas-chromatographic analysis using a dimethylsulfolane column operated at 30 °C showed the main impurities to be methylcyclopentane and 3-methylpentane for a total amount of 0.015%. No unsaturates were detected. The nitrous oxide (>99%), supplied by the Takachiho Shoji Co., was degassed and stored under a vacuum through a −120 °C cold trap.

A given amount (2 or 10 ml) of *n*-hexane was transferred into a tube containing a liquid potassium–sodium alloy freshly distilled *in vacuo*. The tube, fitted with a break-off tip, was stored for one week with frequent shaking. The dried sample was then transferred *in vacuo* into a irradiation cell previously baked and sparkled under a vacuum. The irradiation cells were glass tubes 10 mm in o.d., 7 mm i.d., and 15 mm in o.d., and 12 mm in i.d., with break-off tips. The dead space over the solutions was, at the most, 10% of the total volume.

The samples were irradiated in a ^{60}Co facility at a dose rate of 5.50×10^{19} eV g^{-1} h^{-1}.

After the irradiation, non-condensable gases at the temperature of liquid nitrogen were collected and measured by means of a Toepler pump-gas buret device. The hydrogen was removed by pumping the gaseous mixture into a copper oxide furnace at 250—270 °C. The relative amounts of nitrogen and methane were determined by means of a Hitachi RMU-5 mass spectrometer. The total yield of water and alcohols was determined by the sodium-potassium method.4,5) The alcohols were identified gas-chromatographically.

Results and Discussion

The sodium-potassium treatment not only dehydrates the *n*-hexane but also eliminates micromolar amounts of CO_2 and O_2, initially dissolved in the *n*-hexane, which may act as electron scavengers.

The radiolysis of pure *n*-hexane at different total doses was undertaken. The dose dependence of the hydrogen yield from pure *n*-hexane closely resembles that reported previously,6) but the extrapolated initial *G*-value, 5.79±0.05, is the highest ever reported for *n*-hexane and compares well with the recent data on cyclopentane7) and cyclohexane.4) This large *G*-value may be due to the removal of the scavengers initially dissolved in *n*-hexane.

TABLE 1. PRODUCT YIELDS IN THE RADIOLYSIS OF *n*-HEXANE SOLUTIONS OF N_2O

Total dose ($\times10^{20}$ eV/g)	Mole fraction of N_2O N_{N_2O}	$G(H_2)$	$G(N_2)$	$G(ROH)^{a)}$	$\frac{G(ROH)^{a)}}{G(N_2)}$
6.6	1.50×10^{-2}	2.60	3.8	3.9	1.1
1.1	1.25×10^{-2}	3.03	3.6	3.8	1.1
1.1	8.77×10^{-3}	2.90	3.3	b)	—
6.6	7.26×10^{-3}	2.69	3.6	3.3	0.9
1.1	2.53×10^{-3}	3.93	2.4	2.5	1.0
1.1	1.72×10^{-3}	3.85	2.1	b)	—
1.1	6.71×10^{-4}	4.73	1.4	b)	—
1.1	1.69×10^{-4}	4.90	1.0	0.8	0.8
0.55	7.89×10^{-5}	4.99	0.85	b)	—

a) ROH: oxygen-containing-products,
b) Not measured.

The experimental results on *n*-hexane–N_2O systems are collected in Table 1 as a function of the N_2O mole fraction, N_{N_2O}. The oxygen-containing-products detected here are water and small amounts of 2-hexanol and 3-hexanol. The total *G*-value of alcohols is small, 0.1 at $N_{N_2O}=2\times10^{-3}$. The relative amount of 3-hexanol is *ca.* 50% higher than that of 2-hexanol. The formation of water in this system has already been reported.8) Alcohols have not yet been detected. As is shown in Table 1, the total yield of the oxygen-containing-products denoted ROH is in good agreement with that of N_2, within the limits of experimental error. This finding shows that the decomposition of N_2O in liquid *n*-hexane finally leads to N_2 and ROH in the ratio of one-to-one. The following possible schemes of ROH formation through ionic processes may be deduced:

$$n\text{-}C_6H_{14} \longrightarrow C_6H_{14}^+ + e^- \tag{1}$$

$$e^- + N_2O \longrightarrow N_2O^- \tag{2}$$

$$N_2O^- + C_6H_{14}^+ \longrightarrow N_2 + OH + C_6H_{13} \tag{3a}$$

$$\searrow N_2 + H_2O + C_6H_{12} \tag{3b}$$

$$N_2O^- + n\text{-}C_6H_{14} \longrightarrow N_2 + OH^- + C_6H_{13} \tag{4}$$

$$OH + n\text{-}C_6H_{14} \longrightarrow H_2O + C_6H_{13} \tag{5}$$

$$OH^- + C_6H_{14}^+ \longrightarrow H_2O + C_6H_{13} \tag{6}$$

$$\mathrm{OH} + \mathrm{C_6H_{13}} \longrightarrow \mathrm{C_6H_{13}OH} \qquad (7a)$$
$$\searrow \mathrm{C_6H_{12}} + \mathrm{H_2O} \qquad (7b)$$

Since the selective C–H bond scission in both the 2 and 3 positions of *n*-hexane has already been described,[9] the alcohols detected here may be produced *via* Reaction (7a). The above scheme may at least explain the yields of N_2 and ROH arising from the electron scavenging, but not their yields in excess of the expected yield of the electron. The excess yields of N_2 and ROH may be interpreted effectively as:

$$\mathrm{N_2O} + \mathrm{X} \xrightarrow{n\text{-}\mathrm{C_6H_{14}}} \mathrm{N_2} + \mathrm{ROH} \qquad (8)$$

where X may be intermediates other than N_2O^- or an electron which is captured by N_2O, as is shown in Reaction (2). The intermediate, X, is not determined here, but it must finally lead to the formation of N_2 and ROH again in the ratio of one-to-one. To compare the relative importance of Reactions (2) and (8) as a function of N_{N_2O}, the following attempt has been made.

Let $G(H_2)_0$ be the hydrogen yield in the absence of N_2O corrected for the ionic part of the dose effect on the hydrogen yield.[10] The quantity $\varDelta G(H_2) = G(H_2)_0 - G(H_2)$ is a measure of the decrease in the hydrogen yield resulting from the interruption of the ion-electron recombination processes by N_2O according to the following reactions:

$$e^- + \mathrm{C_6H_{14}}^+ \longrightarrow f'\mathrm{H_2}$$
$$e^- + \mathrm{N_2O} \longrightarrow \mathrm{N_2O^-}$$
$$\mathrm{N_2O^-} + \mathrm{C_6H_{14}}^+ \longrightarrow f''\mathrm{H_2}$$

in which f' and f'' are the efficiencies of hydrogen formation. According to Schuler *et al.*,[11] the efficiency $f'-f''$ for hydrogen formation from *n*-hexane is 0.9. The ratio $\gamma = 0.9G(N_2)/\varDelta G(H_2)$ is approximately the yield of N_2 formed per electron scavenged. If only the above processes (1)—(7b) were to be taken into account, we should expect the value $\gamma \sim 1$. As is shown in Fig. 1, though, the value of γ systematically exceeds 1. This can not be explained solely by Processes (1)—(7b), although this conclusion seems to be less rigorous at very low concentrations because of the large experimental errors. A satisfactory explanation of the excess nitrogen, that is, an intermediate X in Reaction (8), seems to be required.

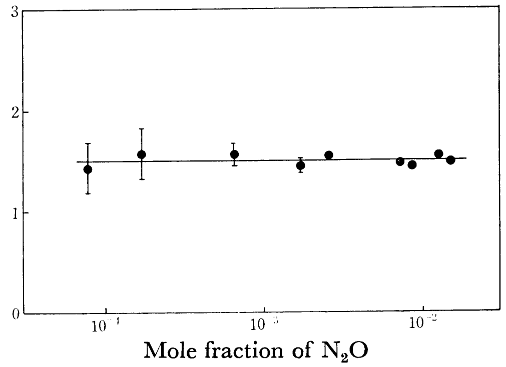

Fig. 1. The ratio γ as a function of the mole fraction of nitrous oxide.

Nitrous oxide appears to be inert towards thermal hydrogen atoms and alkyl radicals. The possibility of a reaction between hydroxyl radical and N_2O is also unlikely.[4] The decomposition of N_2O *via* energy transfer from an excited *n*-hexane molecule does not seem a significant process at least at the lower solute concentrations used here. The same reasoning can be appplied to the proposed[3] secondary reaction between N_2O and its negative ion. If such a reaction had to take place even at the lower concentrations as a significant competing process with Reaction (4), its rate constant would have to be exceedingly high. Among other possibilities deserving further study, the reactions with slow electrons not captured by N_2O or with positive ions may be the most promissing.

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10) Although the precise value of the correction for *n*-hexane has not yet been determined, the values for cyclohexane[11] have been used as an approximation.

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