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Methane Formation in the Radiolysis of Neopentane and Isooctane

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The formation of methane and hydrogen in the γ-radiolysis of neopentane and isooctane has been studied in the presence of an electron scavenger (N_2O) and/or a radical scavenger (styrene). The G-value of nitrogen from neopentane solutions of nitrous oxide was found to be about twice the sum of the decrease in the G-values of methane and hydrogen. From isooctane solutions, $G(N_2)$ was more than three times the sum of the decrease in $G(H_2)$ and $G(CH_4)$. This can be interpreted on the assumption that a significant part of the neutralization of isooctane ions with electrons induces the fragmentation into C_4-hydrocarbons. It was also found that a part of the methane formed (0.9 G in neopentane and 0.2 G in isooctane) was not produced by the reactions of ions or methyl radicals, but by a "molecular" process, probably the decomposition of the highly-excited states.

Because of its large G-value, the formation of hydrogen in the radiolysis of liquid hydrocarbons has been studied by many investigators in an attempt to clarify the primary process of the radiation-induced reactions.[1,2] In the case of branched hydrocarbons, it is well known that methane formation is important and that the G-value of methane increases with the increase in the number of the branched chain.[3] Several papers have reported on the effect of electron scavengers on the G-value of the formation of methane.[4,5] However, the mechanism of the formation of methane has not been discussed systematically in connection with the primary process.

Neopentane and isooctane are typical branched hydrocarbons, and their radiolyses have been studied by several groups.[6-9] Recently, Tanno and his collaborators investigated the fragmentation process of the radical ions produced in the radiolysis of branched hydrocarbons, including neopentane and isooctane.[10,11] In this paper, we will report on the effect of electron and radical scavengers on the G-values of methane and hydrogen, and will discuss the mechanism of the formation of these products.

Experimental

The neopentane (Matheson Co., pure grade) was used as supplied. The isooctane (Tokyo Kasei Co., spectro grade) was used after passing it through a 1-m silica gel column. Gaschromatographic analysis showed that both hydrocarbons contained impurities of less than 0.01%. The nitrous oxide and sulfur hexafluoride (Matheson Co., pure grade) were used after bulb-to-bulb distillations. The styrene monomer (Tokyo Kasei Co., pure grade) was distilled *in vacuo* before use.

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[1] J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

[2] J. M. Warman, K. -D. Asmus and R. H. Schuler, Advances in Chemistry Series, **82**, 25 (1968).

[3] H. Yamazaki and S. Shida, *Isotopes and Radiation* (Tokyo) **2**, 119 (1959).

[4] K. Shinsaka and S. Shida, This Bulletin, **40**, 2796 (1967).

[5] R. A. Holroyd, Advances in Chemistry Series, **82**, 488 (1968).

[6] W. H. Taylor, S. Mori and M. Burton, *J. Amer. Chem. Soc.*, **82**, 5817 (1960).

[7] R. A. Holroyd, *J. Phys. Chem.*, **65**, 1352 (1961).

[8] J. A. Knight, R. L. McDaniel, R. C. Palmer and F. Sicilio, *ibid.*, **65**, 2109 (1961).

[9] T. Kudo and S. Shida, *ibid.*, **67**, 2871 (1963).

[10] K. Tanno, T. Miyazaki, K. Shinsaka and S. Shida, *ibid.*, **71**, 4290 (1967).

[11] K. Tanno, S. Shida and T. Miyazaki, *ibid.*, **72**, 3496 (1968).

Irradiation samples were prepared by repeated freeze-and-thaw cycles. The samples (2 or 10 ml), sealed in glass tubes, were irradiated by ^{60}Co-γ rays at a dose rate of 1.25×10^6 R/hr. All the additives were assumed to be completely soluble, because the gas-phase volume above the irradiation liquid was less than a half of the liquid volume.

Non-condensable gas at 77°K was collected by a Toepler pump, and its amount measured by means of a gas buret. A cuprous oxide furnace at 240°C was used to combust hydrogen into water, which is condensable in a liquid nitrogen trap. The remainder (methane and nitrogen) was analyzed by gas-chromatography. The column used contained activated charcoal (2 m).

Results and Discussion

Neopentane. As is shown in Fig. 1, the G-value of nitrogen increased with an increase in the concentration of nitrous oxide and did not attain a limiting value even at 0.8 mol/l, the highest concentration examined. This is a typical trend observed in the charge scavenging. The G-values of methane and hydrogen decreased with an increase in the concentration of nitrous oxide and seemed to level off at 2.6 and 0.8 respectively. However, these values may be somewhat underestimated because the irradiation dose used for the data in Fig. 1 is not low enough to disregard the build-up of radical scavengers such as isobutene during the radiolysis.[7] The data shown in Table 1 were obtained with much lower irradiation doses. Obviously, the G-value of hydrogen is very much dependent upon the dose, as has already been reported by Holroyd.[7] The dose dependence of $G(CH_4)$ was, however, found to be small. This is consistent with the observation of Holroyd. Therefore, the decreases in the G-values of methane and hydrogen in the presence of 0.4-mol/l N_2O may be estimated to be 0.9 ($=3.5-2.6$) and 0.8 ($=2.2-1.4$) respectively. The sum of these values ($0.9+0.8$) is nearly equal to a half of the G-value of nitrogen (3.6/2) from a 0.4-mol/l N_2O solution.

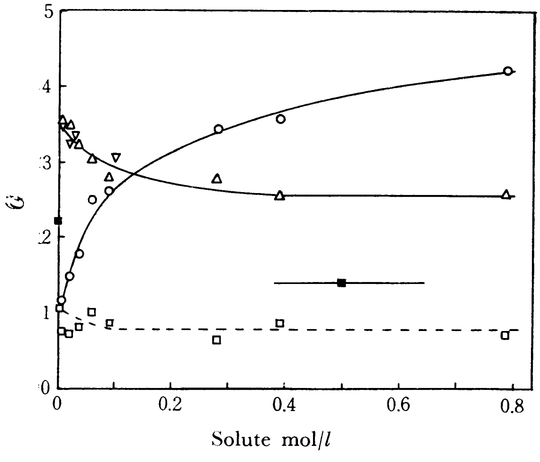

Fig. 1. G-Values of nitrgen (○), methane (△) and hydrogen (□) from neopentane solutions of nitrous oxide and the G-value of methane (▽) from SF_6 solutions. The irradiation dose is 2.0×10^{20} eV/ml except for (■) which is $G(H_2)$ obtained with the irradiation dose of 1.7×10^{18} eV/ml.

Table 1. Dose dependence of $G(H_2)$ from a neopentane solution

Additive	Irradiation dose 10^{18} eV/ml	$G(H_2)$
None	1.1	2.2
	1.7	2.2
	78	1.2
	115	1.1
0.4 mol/l N_2O	1.7	1.4

The effect of sulfur hexafluoride was also examined. The results are plotted in Fig. 1. The effects of the two electron scavengers on the G-value of methane are almost the same. This observation is compatible with the conclusion that the electron scavenging process in the radiolysis of cyclohexane is diffusion-controlled.[12]

Table 2. The effect of styrene monomer on the G-values of products from neopfntane solutions of nitrous oxide

N_2O mol/l	Styrene mol/l	$G(H_2)$	$G(CH_4)$	$G(N_2)$
0	0.43	0.63	1.04	0
0.52	0.26	0.66	1.24	3.97
0.53	0.43	0.64	0.91	3.98
0	0.086	0.85	1.50	0

Use was made of the styrene monomer as a radical scavenger. As is shown in Table 2, the G-values of methane and hydrogen decreased rapidly with an increase in the concentration of styrene and leveled off at 0.9 and 0.6 respectively, while the G-value of nitrogen was not affected by the presence of styrene. These results suggest that the main precursor of methane is the methyl radical, whose G-value is estimated to be 2.6 ($=3.5-0.9$). Holroyd and Klein experimented with the radiolysis of neopnetane in the presence of iodine and found the G-value of methyl iodide to be 2.3.[13] The decrease in $G(H_2)$ from 2.2 to 0.6 due to the presence of styrene may be explained similarly. The difference, $\Delta G=1.6$, probably corresponds to the G-value of the thermal hydrogen atoms produced.

According to Tanno *et al.*,[10] primarily-produced

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[12] S. Sato, T. Terao, M. Kono and S. Shida, This Bulletin, **40**, 1818 (1967).

[13] R. A. Holroyd and G. W. Klein, *J. Amer. Chem. Soc.*, **87**, 4983 (1965).

parent ions in the radiolysis of liquid neopentane can be classified into two types. One consists of highly-excited ions which decompose instantaneously into a methyl radical and a *t*-butyl ion, even in the liquid phase; the other consists of stable neopentane ions which are subject to charge neutralization. They estimated the *G*-value of the former process to be 1.0.

On the basis of the results presented above, we have tentatively constructed the following reaction mechanism for the formation of methane and hydrogen:

$$(CH_3)_3CCH_3 \rightsquigarrow (CH_3)_3C^+ + CH_3 + e^- \qquad (1) \quad G\sim 1.0$$

$$\rightsquigarrow (CH_3)_3CCH_3^+ + e^- \qquad (2) \quad \sim 2.2$$

$$\rightsquigarrow CH_4 + (CH_3)_2C{=}CH_2 \qquad (3) \quad \sim 0.9$$

$$\rightsquigarrow H_2 + \text{residue} \qquad (4) \quad \sim 0.6$$

$$(CH_3)_3CCH_3^+ + e^- \rightarrow (CH_3)_3C + CH_3 \qquad (5) \quad \sim 1.6$$

$$\rightarrow (CH_3)_3CCH_2 + H \qquad (6) \quad \sim 0.6$$

$$(CH_3)_3C^+ + e^- \rightarrow H + (CH_3)_2C{=}CH_2 \qquad (7) \quad \sim 1.0$$

$$CH_3 + (CH_3)_3CCH_3 \rightarrow CH_4 + (CH_3)_3CCH_2 \qquad (8)$$

$$H + (CH_3)_3CCH_3 \rightarrow H_2 + (CH_3)_3CCH_2 \qquad (9)$$

Here, the numbers shown after each reaction are the estimated *G*-values. When nitrous oxide is present in the system, nitrogen becomes an important product. As has been assumed in the radiolysis of the N_2O - cyclohexane solution, if *G*-(N_2) is twice the *G*-value of electrons scavenged by N_2O,[12] the $G(N_2)$ from the N_2O - neopentane solution should be equal to twice the sum of the decreases in $G(CH_4)$ and $G(H_2)$ for according to the above mechanism, each electron should produce a methyl radical or a hydrogen atom when they are neutralized. In fact, this relationship was observed, as has already been stated.

The reactions (3) and (4) are very tentative at present. In their studies of the radiolysis of olefins, Hatano and his collaborators discovered that hot-hydrogen-atom reactions play an important role in the formation of hydrogen and suggested that reactive species are formed from the superexcited state of the olefin.[14] In the radiolysis of neopentane, therefore, the corresponding reactive species might be hot methyl radicals and hot hydrogen atoms, which in turn give rise to the reactions (3) and (4).

Isooctane. Exactly the same experiments as those of neopentane were done with isooctane. The results are shown in Figs. 2 and 3 and in Table 3.

The isooctane molecule has two C–C bonds, whose splitting does not lead to the formation of a methyl radical. This is an essential difference from neopentane when considering the formation of methane. According to Tanno *et al.*,[10] highly-excited isooctane ions decompose into C_4-fragments, but the *G*-value is reported to be only 0.36. On the other hand, the *G*-values of isobutane and isobutene from isooctane have been reported to be about 3.0.[8] One of the possible origins is the following neutralization reaction:

$$iso\text{-}C_8H_{18}^+ + e^- \rightarrow t\text{-}C_4H_9 + iso\text{-}C_4H_9 \qquad (10)$$

If so, the *G*-value of the electrons consumed for this reaction is estimated to be 1.1 (=3.0/2−0.36).

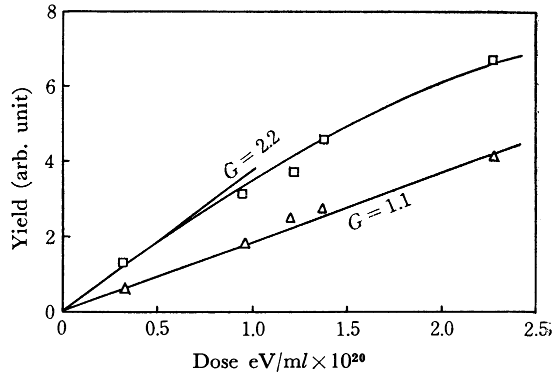

Fig. 2. Irradiation does dependence of *G*-values of hydrogen (□) and methane (△) from isooctane.

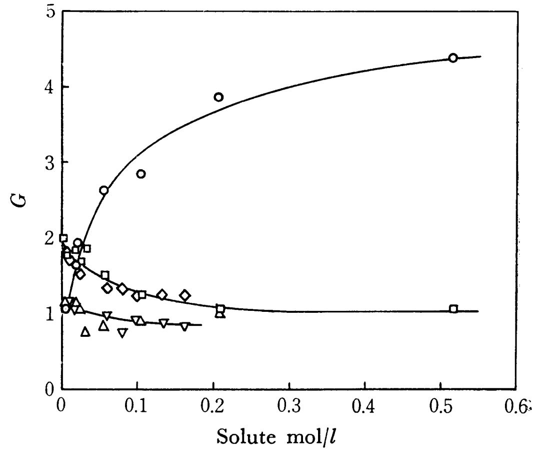

Fig. 3. *G*-Value of nitrogen (○), hydrogen (□) and methane (△) from isooctane solutions of nitrous oxide and *G*-values of hydrogen (◇) and methane (▽) from SF_6 solutions. The irradiation dose is 1.5×10^{20} eV/m*l*.

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[14] Y. Hatano, S. Shida and S. Sato, This Bulletin, **41**, 1120 (1968).

TABLE 3. THE EFFECT OF STYRENE MONOMER ON THE G-VALUES OF GASEOUS PRODUCTS FROM ISOOCTANE SOLUTIONS OF NITROUS OXIDE

N_2O	Styrene	$G(H_2)$	$G(CH_4)$	$G(N_2)$
mol/l				
0	0.43	0.83	0.38	0
0.52	0.43	0.70	0.23	4.6

As is shown in Fig. 3, the decrease in $G(H_2+CH_4)$ due to the presence of electron scavengers is about 1.2 and the corresponding G-value of nitrogen is more than 4.0. If $G(N_2)$ is equal to twice the G-value of the electrons scavenged by nitrous oxide, the following reaction mechanism may be constructed:

$$
\begin{array}{llll}
\text{iso-}C_8H_{18} & \rightsquigarrow C_4H_9^+ + C_4H_9 + e^- & (11) & \sim 0.4 \\
 & \rightsquigarrow C_8H_{18}^+ + e^- & (12) & \sim 3.1 \\
 & \rightsquigarrow H_2 + \text{residue} & (13) & \sim 0.7 \\
 & \rightsquigarrow CH_4 + \text{residue} & (14) & \sim 0.2 \\
C_8H_{18} + e^- & \rightarrow 2C_4H_9 & (10) & \sim 1.1 \\
 & \rightarrow CH_3 + C_7H_{15} & (15) & \sim 0.9 \\
 & \rightarrow H + C_8H_{17} & (16) & \multirow{2}{*}{$\left.\begin{array}{l}\\ \\ \end{array}\right\}\sim 1.5$} \\
C_4H_9^+ + e^- & \rightarrow H + C_4H_8 & (17) &
\end{array}
$$

Here, the G-value of the electrons was assumed to be 3.5 in order to make the G-values of the products self-consistent. The reactions (13) and (14) are tentative as the reactions (3) and (4) in the radiolysis of neopentane.