BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3728—3740 (1970)

The γ-Radiolysis of Liquid *n*-Hexane. The Effects of Radical, Electron, and Positive-ion Scavengers

Kyoji SHINSAKA and Shoji SHIDA

Laboratory of Physical Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo

(Received June 23, 1970)

The effects of various additives, SF_6, NH_3, C_2H_5OH, N_2O, NO, SO_2, and C_2H_4, on the product yields in the γ-radiolysis of liquid *n*-hexane at room temperature have been investigated. The following conclusions have been drawn: (i) The added SO_2 acts mainly as a radical scavenger. (ii) The added NO shows not only the effect of radical scavenging, but also other effects. Therefore, it is inadequate to use NO as a simple radical scavenger. (iii) The C_7-C_{12} products are formed from a combination reaction of alkyl radicals, but not from an ion-molecule reaction. (iv) The formation of $C_6H_{13}^+$ ions by the direct action of radiation is suggested. (v) The *G*-value of ionization is evaluated to be 4.0. A brief discussion concerning the formation of N_2 in the presence of N_2O is also given.

One of the methods of investigating the radiation chemistry of liquid hydrocarbons is the scavenger technique. This method aims at elucidating the mechanism of radiolysis from the effect of additives, which react selectively with radicals or charged species produced by irradiation, on the yields of the radiolytic products. Product analysis, however, has usually been carried out on fragment products. Thus, in the case of alkane radiolysis, there have been only a few works in which the effects of scavengers for charged species on the product yields, including those of olefins and of dimeric paraffins, have been investigated. Consequently, there remain several unsolved problems even in the radiolysis of *n*-hexane, which has been widely investigated by many researchers[1–7] as a typical liquid paraffin. For

---

[1] L. Kevan and W. F. Libby, *J. Chem. Phys.*, **39**, 1288 (1963).

[2] H. A. Dewhurst, *J. Phys. Chem.*, **62**, 15 (1958).

[3] H. Widmer and T. Gäumann, *Helv. Chim. Acta*, **46**, 2766 (1963).

[4] T. J. Hardwick, *J. Phys. Chem.*, **64**, 1623 (1960).

[5] T. Gäumann and B. Reipso, *Advan. Chem. Series*, **82**, 441 (1968).

[6] A. Menger and T. Gäumann, *Helv. Chim. Acta*, **52**, 2129 (1969).

[7] A. Menger and T. Gäumann, *ibid.*, **52**, 2477 (1969).

example, there are two views concerning the mechanism of the formation of dodecanes; one[1] attaches importance to the ion-molecule reaction, and the other,[4] to the combination reaction of hexyl radicals.

In order to clarify the problems, it appears suitable to investigate the effect of additives on the yields of products, including hexenes and dodecanes. The additive should be carefully selected in such a way that it scavenges selectively one reactive species. Thus, SF_6,[8] which is often used as an electron scavenger, and NH_3[9] and C_2H_5OH,[10] which are often used as proton scavengers, appear to be suitable in view of their physical and chemical properties. In order to investigate the radical processes, a pertinent radical scavenger is necessary. For this purpose, SO_2 is tentatively chosen in view of its physical and chemical properties, although there is a possibility that SO_2 scavenges an electron due to its electron affinity ($EA(SO_2) = ca.\ 1$ eV[11]). SO_2 shows a much higher reactivity to alkyl radicals (the rate constant of addition to methyl radicals is $5.0 \times 10^6 M^{-1}$ sec^{-1} at 25°C[12]) than that of ethylene, which is known as an effective hydrogen atom scavenger,[13] a higher ionization potential (IP(SO_2) = 12.34 eV[14]) than that of *n*-hexane (IP(*n*-hexane) = 10.17 eV[15])), and a much higher solubility in *n*-hexane than that of oxygen, which has been often used as an effective radical scavenger. There are few cases, at most, in which SO_2 has been used as a radical scavenger; to the authors' knowledge, the only example seems to be the work by Henglein *et al.*[16] They regarded SO_2 as a radical scavenger on the basis of the fact that the *G*-values of the SO_2 absorbed in the radiolysis of various liquid hydrocarbons were nearly equal to the radical yields determined with DPPH or I_2.

In a previous work,[17] the present authors used N_2O and NO as an electron scavenger and a radical scavenger respectively. With regard to NO, however, it has been pointed out that this is apt to undergo a charge-transfer reaction[18] due to its ionization potential (IP(NO) = 9.25 eV[14]) being lower than that of *n*-hexane, and that it is also apt to form ionic addition products.[19] As for N_2O, the relation of the N_2 yield to that of the electron is still unclear. Therefore, N_2O and NO are again used in order to obtain more information on their effects.

Experimental

Materials. Research-grade *n*-hexane obtained from the Phillips Petroleum Co. was purified for the analysis of the C_7–C_{12} products by passing it through silica-gel, soda-asbestos, and magnesium perchlorate columns, besides the usual purification of freeze-pump-thaw cycles, as has been described in a previous paper;[17] it was purified for the analysis of H_2 and C_1–C_6 products, and N_2 in the presence of N_2O, by only the usual freeze-pump-thaw cycles, for the H_2 yield from the radiolysis of *n*-hexane purified by the latter, more convenient way was the same as the result of the former purification. The purity of *n*-hexane was determined to be more than 99.98% by gas chromatography. The additives were all commercially obtained. SF_6 (minimum purity: 98.0%) obtained from the Matheson Co.; N_2O(99.9%), NH_3(99.5%), SO_2(98.0%), NO(99.9%), and C_2H_4-(99.8%) obtained from the Takachiho-shoji Co., and C_2H_5OH(99.5%) obtained from the Wako-junyaku-kogyo Co. were used after the usual degassing by freeze-pump-thaw cycles. For C_2H_5OH, a further purification to remove a trace of dissolved water was carried out by mixing the ethanol with powder cupric sulfate which was degassed and thoroughly dehydrated.

Sample Preparation and Irradiation. The samples were prepared in the way which has been described before[17] except that the amount of *n*-hexane used for the analysis of H_2, the C_1–C_6 products, and N_2 was 5 cc; it was measured by a pipet, degassed by the usual freeze-pump-thaw cycles, and led into a glass ampoule fitted with a break-off seal. The samples were irradiated at room temperature by a ^{60}Co γ-source either at a dose rate of 6.67×10^{19} eV/g·h to a total dose of 8.0×10^{20} eV/g for the analysis of the C_7–C_{12} products, or at a dose rate of 5.85×10^{19} eV/g·h to a total dose of 5.85×10^{19} eV/g for the analysis of the H_2 and C_1–C_6 products, and of N_2 in the presence of N_2O, unless otherwise specified. In estimating the dose rates, a $G(Fe^{3+})$ value of 8.2 in the Fricke dosimeter saturated with nitrogen was used with the electron-density correction.

Analysis. The analysis of noncondensable gases at −196°C was carried out in the same way as has been described in the previous paper.[17] The C_2–C_{12} products were analyzed gas chromatographically. For the analysis of the C_2–C_6 products, the residual liquid after the analysis of noncondensable gases was sealed in a new glass ampoule under a vacuum at −196°C. Immediately after breaking the seal of the ampoule, a fixed volume of the contents was injected, by means of a micro-syringe, into a gas chromatograph equipped with a flame ioniza-

---

[8] G. Sholes and M. Simic, *Nature*, **202**, 895 (1964).

[9] W. R. Busler, D. H. Martin and F. Williams, *Discuss. Faraday Soc.*, **36**, 102 (1963).

[10] J. W. Buchanan and F. Williams, *J. Chem. Phys.*, **44**, 4377 (1966).

[11] K. Kraus, W. M. -Duysing and H. Neuert, *Z. Naturforsch.*, **16a**, 1385 (1961).

[12] A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, **63**, 2708 (1967).

[13] R. A. Holroyd, *J. Phys. Chem.*, **70**, 1341 (1966).

[14] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[15] W. C. Price, R. Bralsford, P. V. Harris and R. Ridley, *Spectrochim. Acta*, **14**, 45 (1959).

[16] A. Henglein, K. Heine, W. Hoffmeister, W. Schnabel, C. Schneider and H. Url, *Proc. Second Intern. Conf. Peaceful Uses Atomic Energy, United Nations, Geneva*, **29**, 206 (1958).

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

[18] G. G. Meisels, *J. Chem. Phys.*, **42**, 3237 (1965).

[19] P. Kebarle, R. M. Haynes and S. Searles, "Ion-Molecule Reactions in the Gas Phase," Amer. Chem. Soc. Pub., Washington, D. C. (1966) p. 210.

tion detector. An 11-m column with 20% dimethylsulfolane on 60/80 mesh Neosorb NP was used at room temperature (*ca.* 20°C). This column could not resolve *trans*-2-hexene and *cis*-3-hexene so as to allow separate values to be quoted for their yields; therefore, the total yield of these products was determined. After the gas chromatogram of an irradiated sample had been obtained, the same operation was repeated with a reference sample which contained a known quantity of each product component in a fixed quantity of *n*-hexane (nearly as much as in the irradiated sample). The product yields were determined by comparing the peak area of a gas chromatogram of the irradiated sample with that of the reference sample. In this method there was a possibility that a part of the low-molecular-weight products, such as ethane, ethylene, propane, and propylene, escaped into the air during the period from the break of the ampoule to the injection of the sample into the gas chromatograph. This fear could, however, be excluded because the dose dependence of the yields of the fragment products obtained by this method was reasonable; that is, the yields of ethane and propane showed no dose dependence, while the yields of ethylene and propylene indicated the dose dependence that these yields decreased with an increase in the dose. In the presence of a large quantity of an additive which does not dissolve so much in *n*-hexane, the low-molecular-weight product yields obtained by the above method may be somewhat inferior in accuracy to the case without additives, because the time required from the break of the ampoule to the injection of the sample into a gas chromatograph is a little longer than in the case without additives. The C_7–C_{12} products were analyzed in almost the same manner as were the C_2–C_6 products after the irradiated ampoule, without having been submitted to the analysis of noncondensable gases, had been broken open. A 5-m column with 25% Silicone DC 550 on 60/80 mesh Shimalite was used at 130°C. Under these conditions, *iso*-peaks were normally obtained for each hydrocarbon product, one corresponding to the *n*-isomer, and the other, to branched-chain isomers. The *iso*-C_7 peak was not resolved from the tail of the *n*-hexane peak; therefore, the yield of *iso*-C_7 has not been included in the results. Similarly, the *n*-C_{11} peak was not resolved from the *iso*-C_{12} peak and the *iso*-C_{11} peak was not determined quantitatively because the *iso*-C_{11} peak overlapped with that of an impurity peak. These product yields, however, contribute little to the C_7–C_{12} product yields. The C_7–C_{12} products were identified by using authentic samples and by comparison with the results of Widmer *et al.*[3]

Additive Concentration. There seem to be no data showing the solubility of SF_6, N_2O, and NO in *n*-hexane. However, on the assumption that the solubilities of SF_6 and N_2O in *n*-hexane are similar to the case of *n*-heptane,[20,21] in which the solubilities of SF_6 and N_2O have been reported, more than 95% of the amount of added SF_6 and more than 97% of the amount of added N_2O, respectively, were calculated to dissolve in the liquid phase of *n*-hexane in view of the fact that the volume of the gas phase in an irradiated ampoule was less than one-tenth of the total inner volume. On the other hand, it was confirmed that it was easy to dissolve C_2H_5OH in *n*-hexane, and it has been shown that SO_2[22] dissolves very much in *n*-hexane and that C_2H_4[23] dissolves also to about the same degree of N_2O in *n*-heptane. All the concentrations of the additives were estimated by assuming that the additives dissolved completely in the liquid phase of *n*-hexane, for the solubilities of the additives in *n*-hexane would not differ very much from those in *n*-heptane. This assumption is adequate except for the case of the addition of NO, whose concentration in *n*-hexane was estimated to be a few tens of percent less than the value calculated from the assumption of complete dissolution in view of the solubility of NO[21] in cyclohexane.

Results

The results obtained regarding the dose dependence of the C_6–C_{12} product yields from the radiolysis of *n*-hexane are as follows. The hexene yields decrease with an increase in the dose, the degree of the decrease depending on the type of hexene isomer. The dose dependence of hexene yields is very conspicuous in 1-hexene and *trans*-2-hexene+*cis*-3-hexene,[*1] and weak in *cis*-2-hexene and *trans*-3-hexene. The yields of the C_7–C_{12} products, however, show no dose dependence within doses up to 8.0×10^{20} eV/g. The difference between the dose dependence of the hexene yields and that of the C_7–C_{12} product yields will be briefly discussed later. The *G*-values of the products obtained at the total dose of 5.85×10^{19} eV/g and at room temperature are shown in Tables 1 and 2, along with the results of other previous investigations.[1,3,4] The *G*-values in this work, shown in these tables, may be regarded as almost the initial values in view of the dose dependence of the hexene yields; they agree well with the results given by Widmer *et al.*[3] except for somewhat larger differences in the cases of ethane, ethylene, and propane. The ratio of the total number of carbon atoms to that of the hydrogen atoms calculated, respectively, from the *G*-values in Tables 1 and 2 is 0.420; this agrees well with the ratio in an *n*-hexane molecule, *i. e.*, 0.429. The

---

20) L. C. Yen and J. J. Mcketta, Jr., *J. Chem. Eng. Data*, **7**, 288 (1962).

21) G. Archer and J. H. Hildebrand, *J. Phys. Chem.*, **67**, 1830 (1963).

22) "Solubilities of Inorganic and Organic Compounds," Vol. 1, ed. by H. Stephen and T. Stephen, Pergamon Press, London (1963) p. 970.

23) *Ibid.*, p. 1179.

24) *Ibid.*, p. 921.

[*1] Since the seperate values of *trans*-2-hexene yield and *cis*-3-hexene yield could not be obtained, the total value of these product yields was represented using the plus sign, +. The *cis*-3-hexene yield was calculated to be 0.076—0.17 by using the ratio, *trans*/*cis*=4±1.5 given by Hardwick[4] in regard to 3-hexene, and by using the *trans*-3-hexene yield obtained in this work. Therefore, the total yield of *trans*-2-hexene and *cis*-3-hexene may be regarded almost as the yield of *trans*-2-hexene and the total yield is approximately represented as the *trans*-2-hexene yield in Table 1.

TABLE 1. THE G-VALUES OF HYDROGEN, FRAGMENT PRODUCTS AND HEXENES FROM THE RADIOLYSIS OF LIQUID n-HEXANE

Product	a	b	c	d
H_2	5.01	5.25	5.28	5.09
CH_4	0.18_0	0.15	0.10	
C_2H_6	0.42_3	0.22	0.21	0.50
C_2H_4	0.24_5	0.14	0.23	
C_3H_8	0.41_0	0.31	0.13	0.26
C_3H_6	0.19_3	0.18	0.07	0.07
iso-C_4H_{10}	0			0.02
n-C_4H_{10}	0.35_4	0.36	0.05	0.46
iso-C_4H_8	0			0.02
1-C_4H_8	0.14_0	0.12		0.08
trans-2-C_4H_8	0.01_3	0.01		0.02
iso-C_5H_{12}	0		0.02	0.05
n-C_5H_{12}	0.10_1	0.09		0.12
1-C_5H_{10}	0.03_6	0.04		
trans-2-C_5H_{10}	0.02_1	0.02		
1-C_6H_{12}	0.86	0.64±0.05	0.73	0.46
trans-2-C_6H_{12}	1.23[e)]	11.3±0.07	1.82	1.15
cis-2-C_6H_{12}	0.55	0.43±0.10		0.46
trans-3-C_6H_{12}	0.42	0.34±0.05	0.55	0.13
cis-3-C_6H_{12}				0.04
Total hexane	3.06	2.54	3.10	2.24

a) Obtained in this work. Irradiation with ^{60}Co γ-rays at 5 .85×10^{19} eV/g at room temperature.

b) Obtained by Widmer *et al.*[3)] Initial values. Irradiation with ^{60}Co γ-rays at 25°C.

c) Obtained by Hardwick.[4)] $G(H_2)$, $G(C_6H_{12})$: initial values. The dose for other products is not clear. Electron irradiation at 25°C.

d) Obtained by Kevan *et al.*[1)] $G(H_2)$ obtained at 1.24×10^{19} eV/g. G-values of the fragment products obtained at 16.2×10^{20} eV/g. $G(C_6H_{12})$ obtained at 10.2×10^{20} eV/g. Irradiation with ^{60}Co γ-rays at 20°C.

e) This value shows more exactly the total yield of *trans*-2-hexene and *cis*-3-hexene. See the text.

TABLE 2. THE G-VALUES OF THE C_7-C_{12} PRODUCTS FROM THE RADIOLYSIS OF LIQUID n-HEXANE

Product	a	b	c	d
$2MeC_6$		0.014	0.06	0.61
$3MeC_6$		0.011		
n-C_7H_{16}	0.01_6	0.021		
$3EtC_6$	0.13_4	0.12	0.26	
$3MeC_7$				
n-C_8H_{18}	0.02_8	0.032		
$4EtC_7$	0.09_6	0.036	0.23	
$4MeC_8$		0.048		
n-C_9H_{20}	0.01_9	0.025		
4-EtC_8	0.08_7	0.041	0.27	
5-MeC_9		0.050		
n-$C_{10}H_{22}$	0.01_6	0.023		
$4EtC_9$		0.017	0.02	
$5MeC_{10}$				
n-$C_{11}H_{24}$				
$4,5Et_2C_8$	0.21_5	0.17	1.70	0.20
$4Et5MeC_9$	0.51_0	0.49		0.39
$5,6Me_2C_{10}$	0.31_4	0.32		0.24
$4EtC_{10}$	0.10_2	0.11		0
$5MeC_{11}$	0.13_0	0.14		0.21
n-$C_{12}H_{26}$	0.02_3	0.029		0.025
Total dodecane	1.29	1.26	1.70	1.06

a) Obtained in this work. Irradiation with ^{60}Co γ-rays at room temperature.

b) Obtained by Widmer *et al.*[3)] Initial values. Irradiation with ^{60}Co γ-rays at 25°C.

c) Obtained by Hardwick.[4)] The dose is not clear. Electron irradiation at 25°C.

d) Obtained by Kevan *et al.*[1)] G-values of the C_7-C_{11} products obtained at 16.2×10^{20} eV/g. $G(C_{12}H_{26})$ obtained at 3.38×10^{20} eV/g. Irradiation with ^{60}Co γ-rays at 20°C.

G-value of a net decomposition of n-hexane is defined by the following equations:

$$G_{\mathrm{no}}(-n\text{-}C_6H_{14}) = \sum_{i=1}^{12} iG(C_i)/6 \tag{A}$$

or

$$G_{\mathrm{no}}(-n\text{-}C_6H_{14}) = \sum_{i=1}^{13} 2iG(H_{2i})/14 \tag{B}$$

where $G_{\mathrm{no}}(-n\text{-}C_6H_{14})$ indicates the G-value of the net decomposition of n-hexane, and where $G(C_i)$ and $G(H_{2i})$ indicate the G-values of the products, whose numbers of carbon atoms and hydrogen atoms are i and $2\times i$ respectively. The average, $G_{\mathrm{no}}(-n\text{-}C_6H_{14})$, of the two values obtained by the use of Eq. (A) and Eq. (B) is calculated to be 7.30. The percentage of the decomposition of n-hexane is calculated to be 0.061% at the dose of 5.85×10^{19}

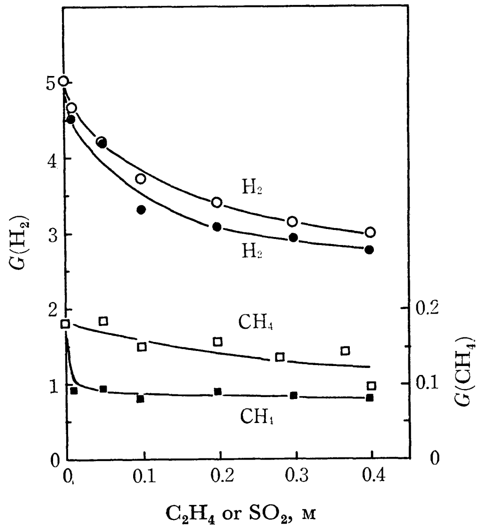

Fig. 1. Yields of H_2 and CH_4 as functions of SO_2 or C_2H_4 concentration.
○, □; C_2H_4 ●, ■; SO_2

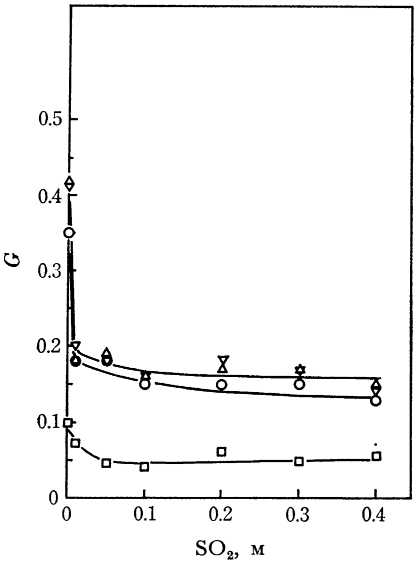

Fig. 2(a). Yields of fragment paraffin products as functions of SO_2 concentration.
Dose: *ca.* 6×10^{19} eV/g
△, C_2H_6 ▽, C_3H_8 ○, *n*-C_4H_{10} □, *n*-C_5H_{12}

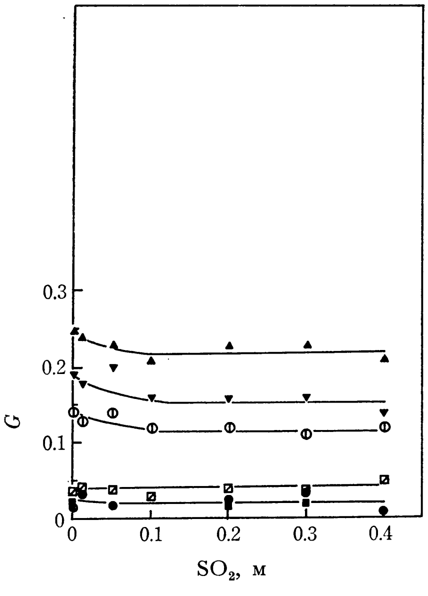

Fig. 2(b). Yields of fragment olefin products as functions of SO_2 concentration.
Dose: *ca.* 6×10^{19} eV/g
▲, C_2H_4 ▼, C_3H_6 ⦶, 1-C_4H_8 ▨, 1-C_5H_{10}
■, *trans*-2-C_5H_{10} ●, *trans*-2-C_4H_8

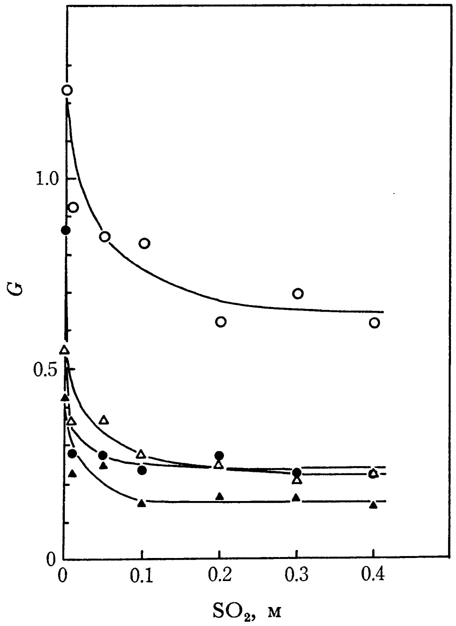

Fig. 2(c). Yields of hexenes as functions of SO_2 concentration.
Dose: *ca.* 6×10^{19} eV/g
○: *trans*-2-C_6H_{12}+*cis*-3-C_6H_{12}, ●: 1-C_6H_{12},
△: *cis*-2-C_6H_{12}, ▲: *trans*-3-C_6H_{12}

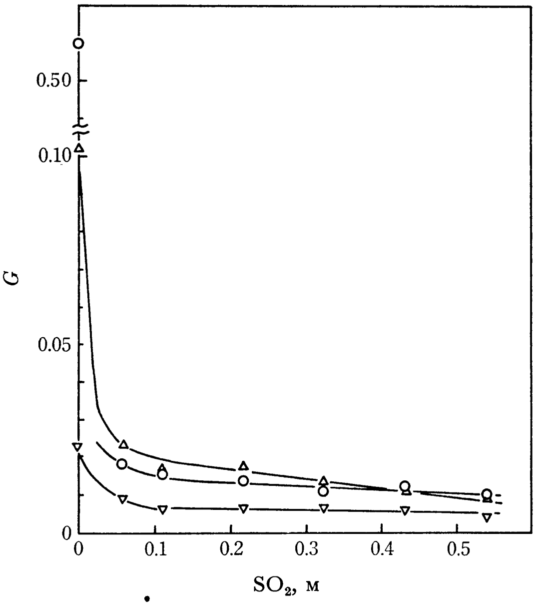

Fig. 2(d). Yields of 4-ethyldecane, 4-ethyl-5-methylnonane and *n*-dodecane as functions of SO_2 concentration.
△, 4EtC$_{10}$ ○, 4Et5MeC$_9$ ▽, *n*-C_{12}

eV/g and 0.84% at the dose of 8×10^{20} eV/g by using this value, 7.30.

The effects of additives on the C_7–C_{12} products were investigated with samples irradiated up to a dose of 8×10^{20} eV/g. This dose is permissible in view of the finding that the C_7–C_{12} product yields showed no dose dependence in the absence of additives and that the C_{12} product yields also showed no dose dependence in the presence of 0.55M N_2O. Figure 1 shows the changes in the *G*-values of hydrogen and methane upon the addition of SO_2, togeth-

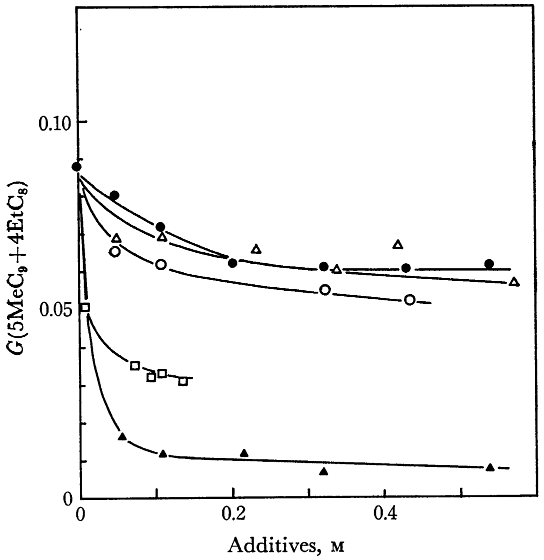

Fig. 3. Yields of 5-methylnonane+4-ethyloctane as functions of concentration of various additives.
●, NH_3 △, C_2H_5OH ○, N_2O □, SF_6 ▲, SO_2

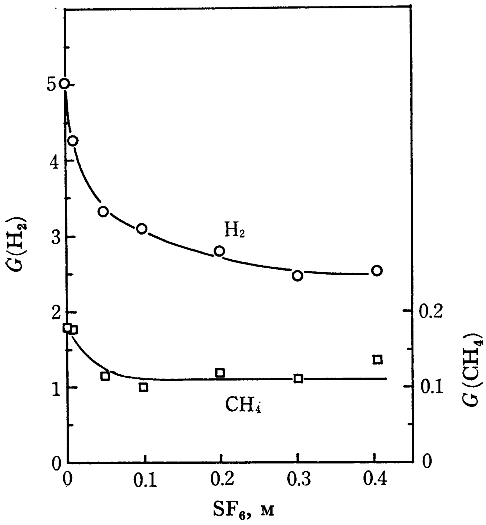

Fig. 4(a). Yields of H_2 and CH_4 as functions of SF_6 concentration.

er with those in the case of the addition of C_2H_4. The change in the G-value of hydrogen in the presence of SO_2 is very similar to that obtained in the presence of C_2H_4. The changes in the G-value of methane are, however, very different for SO_2 and C_2H_4. The G-value of methane decreases drastically to about a half of the initial value at a low concentration of SO_2, and afterward comes to show almost no change. On the other hand, with the concentration of C_2H_4 the G-value of methane gradually decreases.

Figures 2(a) and 2(b) show the changes in the G-values of the other fragment products upon the addition of SO_2. The G-values of the saturated fragment products decrease to about a half of the initial value, or more, upon the addition of SO_2. The G-values of the unsaturated fragment products, however, show only a small decrease. Figure 2(c) shows the changes in the G-values of hexenes upon the addition of SO_2. The G-values of hexenes decrease to about a half of the initial value, or more. Figure 2(d) shows the changes in three kinds of C_{12} products as examples of the effect of the addition of SO_2; the G-values of all the C_{12} products decrease drastically, *e. g.*, to a value less than one-fiftieth of the initial value in 4-ethyl-5-methylnonane (4Et5MeC$_9$ for brevity), which shows the most conspicuous decrease, and to a value less than one-fourth of the

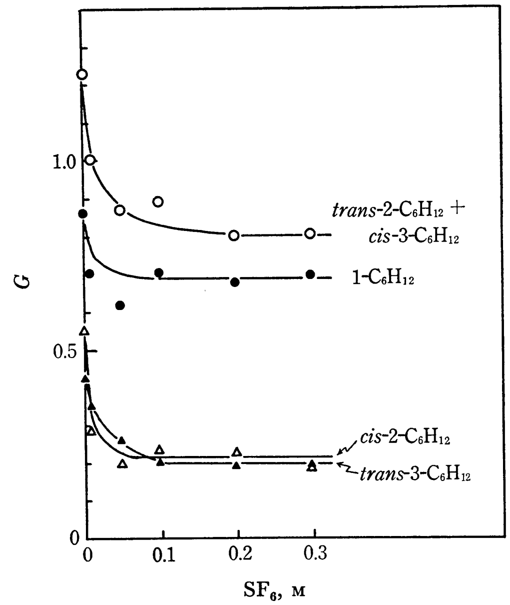

Fig. 4(b). Yields of hexenes as functions of SF_6 concentration.
Dose: *ca.* 6×10^{19} eV/g

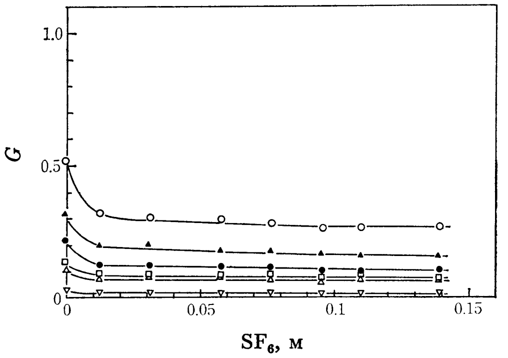

Fig. 4(c). Yields of dodecanes as functions of SF_6 concentration.
○, 4Et5MeC$_9$ ▲, 5,6Me$_2$C$_{10}$ ●, 4,5Et$_2$C$_8$
□, 5MeC$_{11}$ △, 4EtC$_{10}$ ▽, n-C$_{12}$

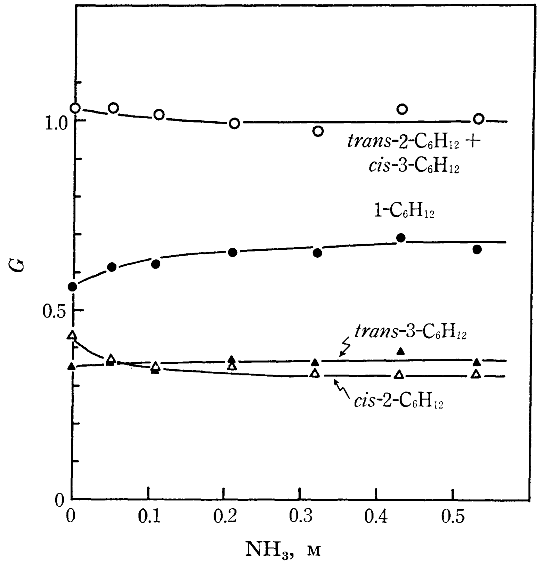

Fig. 5(a). Yields of hexenes as functions of NH_3 concentration.
Dose: 8.0×10^{20} eV/g

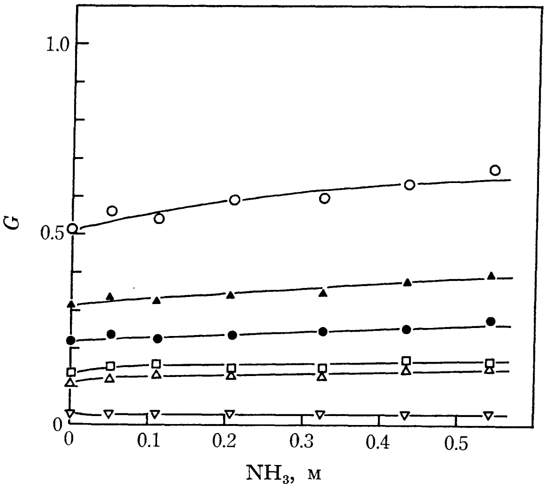

Fig. 5(b). Yields of dodecanes as functions of NH_3 concentration.
○: 4Et5MeC_9, ▲: 5,6Me_2C_{10}, ●: 4,5Et_2C_8, □: 5MeC_{11}, △: 4EtC_{10}, ▽: n-C_{12}

initial value even in *n*-dodecane (*n*-C_{12} for brevity), which shows the smallest decrease. Figure 3 shows the changes in the *G*-value of 5-methylnonane+4-ethyloctane (5MeC_9+4EtC_8 for brevity) as a typical example of the C_7–C_{10} products affected by the addition of SO_2, together with the results of other additives.

Upon the addition of SO_2, the *G*-values of all the C_7–C_{10} products decrease drastically, *i. e.*, to a value less than one-tenth of the initial value in the most conspicuous decrease and to a value less than one-fourth of the initial value even in the smallest

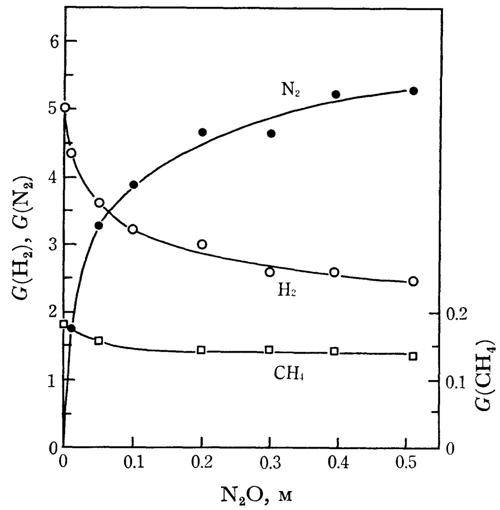

Fig. 6. Yields of H_2, CH_4 and N_2 as functions of N_2O concentration.

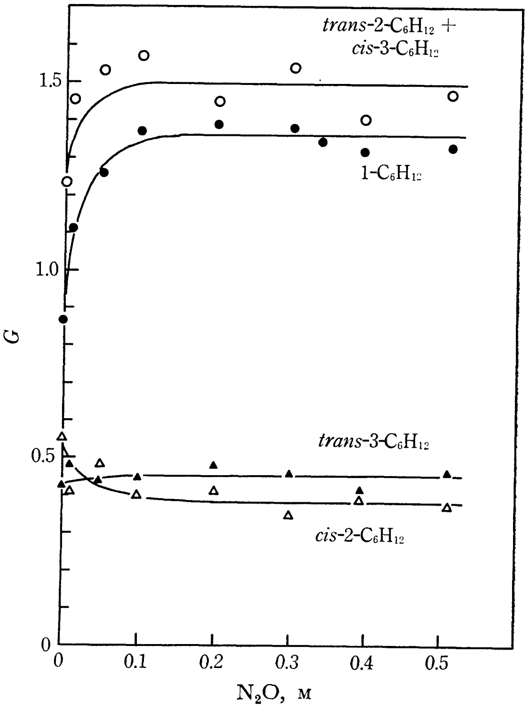

Fig. 7(a). Yields of hexenes as functions of N_2O concentration.

decrease, except for the case of *n*-heptane, whose *G*-value is poorer in accuracy due to its inclusion in the tail of *n*-hexane. Furthermore, the *G*-values of all the C_7–C_{12} products continue to decrease gradually with an increase in the concentration of SO_2 after the initial sharp decrease. Figure 4(a) shows the changes in the *G*-values of H_2 and CH_4 upon the addition of SF_6. Figures 4(b) and 4(c) show the changes in the *G*-values of hexenes and do-

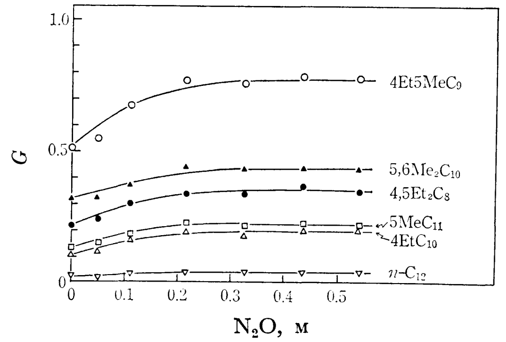

Fig. 7(b). Yields of dodecanes as functions of N_2O concentration.

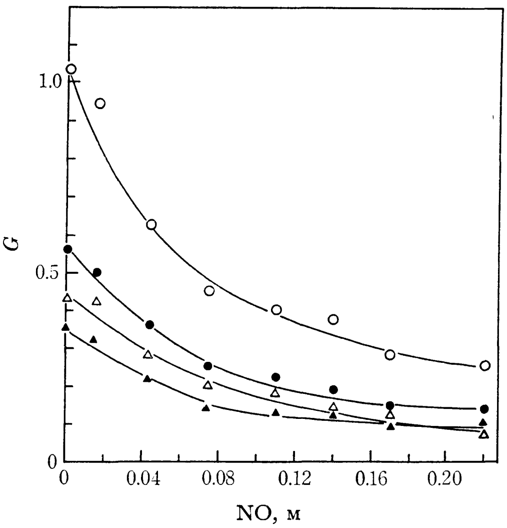

Fig. 8. Yields of hexenes as functions of NO concentration.
Dose: 8.0×10^{20} eV/g
○: *trans*-2-C_6H_{12}+*cis*-3-C_6H_{12}, ●: 1-C_6H_{12},
△: *cis*-2-C_6H_{12}, ▲: *trans*-3-C_6H_{12}

decanes respectively upon the addition of SF_6. As is shown in Figs. 3, 4(a), 4(b), and 4(c), the G-values of all the products decrease to about a half of the initial values, or less, upon the addition of SF_6 and come to show little change at higher concentrations of SF_6.

Figures 5(a) and 5(b) show the changes in the G-values of hexenes and dodecanes upon the addition of NH_3. Though the changes in the G-values of hexenes depend on the kind of hexene, the total G-value of hexenes in the presence of NH_3 is almost equal to that obtained in the absence of the additive. The G-values of the dodecanes increase more or less with the concentration of NH_3. A tendency similar to the changes in the product yields obtained upon the addition of NH_3 is also observed upon the addition of C_2H_5OH. Figure 6 shows the changes in the G-values of H_2, CH_4, and N_2 upon the addition of N_2O. Figures 7(a) and 7(b) show the

Table 3. Effects of additives on the G-values of hydrogen, fragment products and hexenes
Dose: 5.85×10^{19} eV/g

Product	Additive					
	None	SF_6	NH_3	SF_6+ NH_3	SO_2	N_2O
H_2	5.01	2.50	5.53	2.72	2.80	2.45
CH_4	0.18_0	0.11_0	0.14_1	0.15_4	0.08_5	0.14_0
C_2H_6	0.42_3	0.20_0	0.16_0	0.08_2	0.16_0	0.26_0
C_2H_4	0.24_5	0.10_0	0.09_1	0.04_7	0.22_0	0.16_0
C_3H_8	0.41_0	0.26_0	0.24_0	0.13_4	0.16_0	0.28_0
C_3H_6	0.19_3	0.08_5	0.11_0	0.06_6	0.15_5	0.12_0
n-C_4H_{10}	0.35_4	0.25_0	0.22_0	0.15_3	0.14_0	0.24_0
1-C_4H_8	0.14_0	0.07_5	0.11_0	0.07_4	0.11_5	0.09_0
trans-2-C_4H_8	0.01_3	0.01_5			0.02_0	0.01_5
n-C_5H_{12}	0.10_1	0.07_5	0.06_0	0.04_0	0.05_0	0.08_0
1-C_5H_{10}	0.03_6	0.02_5	0.02_8	0.02_8	0.04_0	0.02_5
trans-2-C_5H_{10}	0.02_1	0.04_0			0.02_0	
1-C_6H_{12}	0.86	0.69	0.98	1.14	0.24	1.36
trans-3-C_6H_{12}	0.42	0.20	0.37	0.45	0.15	0.45
trans-2-C_6H_{12}+ *cis*-3-C_6H_{12}	1.23	0.80	1.27	1.38	0.65	1.50
cis-2-C_6H_{12}	0.55	0.22	0.36	0.38	0.22	0.38
Total hexene	3.06	1.91	2.98	3.35	1.26	3.69

Table 4. Effects of additives on the G-values of the C_7-C_{12} products
Dose: 8.0×10^{20} eV/g

Product	Additive					
	None	SF_6	NH_3	SF_6+ NH_3	SO_2	N_2O
n-C_7H_{16}	0.01_6	0.01_1	0.01_8		0.01_0	0.01_6
$3EtC_6$+ $3MeC_7$	0.13_4	0.06_2	0.09_9	0.03_6	0.01_1	0.10_0
n-C_8H_{18}	0.02_8	0.01_6	0.02_0	0.01_3	0.00_6	0.02_0
$4EtC_7$+ $4MeC_8$	0.09_6	0.04_0	0.07_5	0.03_3	0.00_9	0.06_4
n-C_9H_{20}	0.01_9	0.00_9	0.01_4	0.01_9	0.00_5	0.01_4
$4EtC_8$+ $5MeC_9$	0.08_7	0.03_2	0.06_0	0.02_5	0.00_7	0.05_2
n-$C_{10}H_{22}$	0.01_6	0.00_9	0.01_3	0.00_9	0.00_3	0.01_0
$4,5Et_2C_8$	0.21_5	0.10_4	0.27_0	0.09_0	0.00_5	0.34_9
$4Et5MeC_9$	0.51_0	0.26_4	0.65_0	0.20_0	0.01_0	0.77_9
$5,6Me_2C_{10}$	0.31_4	0.15_8	0.39_0	0.11_7	0.00_6	0.43_4
$4EtC_{10}$	0.10_2	0.06_4	0.14_7	0.07_3	0.00_9	0.19_6
$5MeC_{11}$	0.13_0	0.07_2	0.16_5	0.07_5	0.01_1	0.22_0
n-$C_{12}H_{26}$	0.02_2	0.01_5	0.02_6	0.02_1	0.00_5	0.03_8
Total dodecane	1.29	0.67	1.66	0.58	0.05	2.02

Table 5. Effects of added NO and C_2H_5OH in comparison with added SO_2 and NH_3 on the G-values of hexenes and dodecanes
Dose: 8.0×10^{20} eV/g

Product	Additive				
	None	SO_2	NO	NH_3	C_2H_5OH
1-C_6H_{12}	0.56	0.25	0.14	0.68	0.59
trans-3-C_6H_{12}	0.35	0.20	0.10	0.37	0.34
trans-2-C_6H_{12}+ *cis*-3-C_6H_{12}	1.03	0.51	0.25	1.00	0.92
cis-2-C_6H_{12}	0.43	0.16	0.08	0.33	0.33
Total hexene	2.37	1.22	0.57	2.38	2.18
4,5Et_2C_8	0.21_5			0.27_0	0.24_7
4Et5MeC_9	0.51_0			0.65_0	0.55_5
5,6Me_2C_{10}	0.31_4			0.39_0	0.35_1
4EtC_{10}	0.10_2			0.14_7	0.12_0
5MeC_{11}	0.13_0			0.16_5	0.14_1
n-C_{12}	0.02_3			0.02_6	0.02_0
Total dodecane	1.29			1.66	1.43

changes in the G-values of hexenes and dodecanes respectively upon the addition of N_2O. Though the changes in the G-values of hexenes are different, depending on the kind of hexene, the total yield of hexenes increases markedly with the concentration of N_2O. Figure 8 shows the changes in the G-values of hexenes upon the addition of NO. As has been stated before, the actual concentration of NO is estimated to be less than the value indicated in Fig. 8 because of the small solubility of NO. The decrease in hexene yields upon the addition of NO is much larger than that upon the addition of SO_2.

As is shown in the figures given above, the G-values of the products, with some exceptions, generally come to show little change at higher concentrations of the additives. The G-values obtained at sufficiently high concentrations of the additives are tabulated in Tables 3, 4, and 5, together with the data which have not been shown before.

Discussion

i) Effects of SF_6, NH_3, and SO_2. SF_6 is known to scavenge efficiently thermal electrons such as reaction (1):[25]

$$e^- + SF_6 \longrightarrow SF_6^- \qquad (1)$$

On the other hand, SF_6 does not react with a methyl radical, even up to the temperature of 350°C.[26] Consequently, SF_6 added to n-hexane may safely be assumed to act as an electron scavenger, but not to react with radicals. Further, the possibility of a charge-transfer reaction from a parent n-hexane ion to SF_6 can be excluded because the ionization potential of SF_6 (IP=16.15 eV)[27] is much higher than that of n-hexane. SF_6^- can be assumed subsequently to undergo a neutralization reaction with a hydrocarbon ion; this reaction can also be assumed to be such a moderate reaction that it does not cause the decomposition of either ion because of a comparatively high electron affinity of SF_6 (EA=1.49 eV).[28] The major neutralization reaction is shown by reacion (2):

$$SF_6^- + n\text{-}C_6H_{14}^+ \longrightarrow SF_6 + n\text{-}C_6H_{14} \qquad (2)$$

As for the effect of added NH_3, the proton-transfer reaction shown by reaction (3) and the subsequent neutralization reaction, (4), can be assumed for the following reasons.

$$n\text{-}C_6H_{14}^+ + NH_3 \longrightarrow C_6H_{13} + NH_4^+ \qquad (3)$$

$$NH_4^+ + e^- \longrightarrow NH_3 + H \qquad (4)$$

NH_3 has a high proton affinity (PA=8.78 eV).[29] On the other hand, the possibility of the reaction of NH_3 with a hydrogen atom can be excluded because the reaction is very slow ($H+NH_3 \xrightarrow{k} H_2+NH_2$; $k = 2.2 \times 10^2 \text{M}^{-1} \text{sec}^{-1}$, 25°C).[30] Furthermore, the possibility of a charge-transfer reaction from a hydrocarbon ion to NH_3 may be also excluded because the ionization potential of NH_3 (IP=10.15 eV)[31] is almost equal to that of n-hexane (IP=10.17 eV)[15] and because the concentration of NH_3 is 9 mol% at most. The above assumptions concerning the effects of SF_6 and NH_3 are the same as those adopted in other works.[9,32–35]

As was stated in the introduction to this paper, the most likely effect of the added SO_2 is radical scavenging, although there is a possibility that SO_2 also scavenges an electron, as has been shown by Guarino *et al.*[36] They reported that the electron-scavenging efficiency of SO_2 was relatively high in the irradiated matrix of MTHF at −196°C. Their results, however, were obtained very different conditions from this work, so it is inappropriate to use

---

25) D. C. Frost and C. A. McDowell, *J. Chem. Phys.*, **29**, 503 (1958).

26) H. F. Lefevre, J. D. Kale and R. B. Timmons, *J. Phys. Chem.*, **73**, 1614 (1969).

27) E. D. Nostrand and A. B. F. Duncan, *J. Amer. Chem. Soc.*, **76**, 3377 (1954).

28) J. Kay and F. M. Page, *Trans. Faraday Soc.*, **60**, 1042 (1964).

29) A. P. Altschuller, *J. Amer. Chem. Soc.*, **77**, 3480 (1955).

30) C. Willis, A. Boyd and O. A. Miller, *Can. J. Chem.*, **47**, 3007 (1969).

31) K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957).

32) K. Tanno, T. Miyazaki, K. Shinsaka and S. Shida, *J. Phys. Chem.*, **71**, 4290 (1967).

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

34) T. Miyazaki and S. Shida, This Bulletin, **38**, 2114 (1965).

35) T. Miyazaki and S. Shida, *ibid.*, **39**, 2344 (1966).

36) J. P. Guarino, M. R. Ronayne and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).

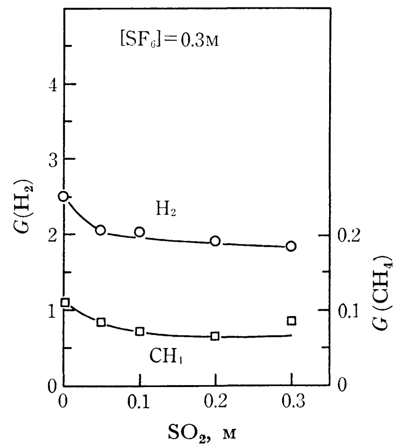

Fig. 9. Yields of H_2 and CH_4 as functions of SO_2 concentration in the presence of 0.3M of SF_6.

their results in the interpretation of the results of this work.

In order to estimate the effect of electron scavenging, the G-values of H_2 and CH_4 from the radiolysis of n-hexane in the presence of SO_2 were compared with those obtained in the coexistence of SO_2 and SF_6. The changes in the G-values of H_2 and CH_4 in the presence of 0.3M of SF_6 with the concentration of SO_2 are shown in Fig. 9. The G-value of H_2 at a sufficiently high concentration of SO_2 in Fig. 9 is 1.85, which is about one unit less than the case in which only SO_2 is added. The difference of one unit can not be explained if SO_2 also acts as an electron scavenger. On the other hand, in the coexistence of 0.3M SO_2 and 0.3M N_2O, the $G(N_2)$ value was determined to be 4.3, while in the presence of 0.3M N_2O only, $G(N_2)$ was 4.9. This small decrease in $G(N_2)$ due to the added SO_2 appears to indicate that the electron-scavenging effect of SO_2 is minor. The similarity in the changes in $G(H_2)$ between the addition of SO_2 and that of C_2H_4 supports the effect of radical scavenging of SO_2, because C_2H_4 in n-hexane can be regarded as an effective hydrogen-atom scavenger.[13] Consequently, the SO_2 added to n-hexane can be regarded mainly as a radical scavenger, and the decreases in the products upon the addition of SO_2 shown in the results may be considered to be brought about by the radical scavenging of SO_2. The sharp decrease in $G(CH_4)$ upon the addition of SO_2 in contrast with the result of the addition of C_2H_4 in Fig. 1 is considered to show that SO_2 is much more effective as a radical scavenger to the methyl radical than is C_2H_4. The C_7–C_{12} products appear to be almost exclusively formed from the combination reaction of alkyl radicals in view of the fact that the addition of SO_2 to n-hexane remarkably decreases the G-values of the C_7–C_{12} products to values ranging from one-fourth to one-fiftieth of the values obtained in the absence of the additives, as is shown in Tables 3 and 4.

The results shown in Tables 3 and 4, which were obtained when SF_6, NH_3 or SO_2 was separately added, can be explained qualitatively in terms of the effects of these additives, as has been mentioned before, assuming the following mechanism of n-hexane radiolysis:

$$\begin{array}{rcll}
 & \nearrow\!\!\!\sim & n\text{-C}_6\text{H}_{14}^+ + e^- & (5) \\
n\text{-C}_6\text{H}_{14} & & & \\
 & \searrow\!\!\!\sim & n\text{-C}_6\text{H}_{14}^* & (6) \\
 & \nearrow & \text{C}_6\text{H}_{13} + \text{H} & (7) \\
n\text{-C}_6\text{H}_{14}^+ + e^- & \longrightarrow & \text{C}_6\text{H}_{12} + \text{H}_2 & (8) \\
 & \searrow & \text{R}_1\text{H} + \text{R}_2\text{H} & (9) \\
 & \nearrow & \text{C}_6\text{H}_{13} + \text{H} & (10) \\
n\text{-C}_6\text{H}_{14}^* & \longrightarrow & \text{C}_6\text{H}_{12} + \text{H}_2 & (11) \\
 & \searrow & \text{R}_1\text{H} + \text{R}_2\text{H} & (12) \\
\text{H} + n\text{-C}_6\text{H}_{14} & \longrightarrow & \text{H}_2 + \text{C}_6\text{H}_{13} & (13) \\
 & \nearrow & \text{R}_1\text{HH} + \text{R}_2 & (14) \\
\text{R}_1\text{H} + \text{R}_2\text{H} & \longrightarrow & \text{R}_1 + \text{R}_2\text{HH} & (15) \\
 & \searrow & \text{R}_1\text{HHR}_2 & (16) \\
 & \nearrow & \text{R}_1\text{HH} + \text{C}_6\text{H}_{12} & (17) \\
\text{R}_1\text{H} + \text{C}_6\text{H}_{13} & \longrightarrow & \text{R}_1 + n\text{-C}_6\text{H}_{14} & (18) \\
 & \searrow & \text{R}_1\text{HC}_6\text{H}_{13} & (19) \\
 & \nearrow & \text{C}_6\text{H}_{12} + n\text{-C}_6\text{H}_{14} & (20) \\
\text{C}_6\text{H}_{13} + \text{C}_6\text{H}_{13} & & & \\
 & \searrow & \text{C}_{12}\text{H}_{26} & (21)
\end{array}$$

where reactions (5) and (6) are the ionization process and the direct-excitation process respectively, and where R_1H and R_2H represent fragment alkyl radicals other than hexyl radicals. Reactions (1) and (2) probably occur instead of reactions (7), (8) and (9) in the presence of SF_6 and cause the decreases in the product yields shown in Tables 3 and 4. On the other hand, reactions (3) and (4) probably occur instead of reactions (7), (8) and (9) in the presence of NH_3.

The results obtained upon the addition of NH_3 can be explained as follows. (i) The small increase in $G(H_2)$ from the value obtained without additives may correspond to the yield by which NH_3 replaces reaction (9) by reactions (3), (4) and (13). (ii) The result that the G-values of the fragment products (from C_1 to C_5) are nearly equal to the values obtained upon the addition of SF_6 may be because reaction (9) is interfered with, as in the case of SF_6. (iii) The result that the total G-value of hexenes is nearly equal to the value obtained in the absence of additives may be explained on the assumption that the decrease in the molecular yield of hexene by reaction (8) is nearly equal to the increase in the hexene yield by the disproportionation reaction (20). (iv) The results that the G-values of the C_7–C_{10} products are somewhat larger than those with SF_6, and that the G-values of dodecanes are somewhat larger than the values obtained in the absence of additives, may be because the increase of hexyl radicals in the presence of

NH_3 twice the yield by which the added NH_3 interferes with reactions (8) and (9).

ii) Dose Dependence of the Product Yields. The difference in the dose dependence between the yields of the hexenes and those of the dodecanes can be explained in the same way as Dewhurst[37] did in the case of cyclohexane. That is, when a hydrogen atom is added to a hexene molecule, as in reaction (22), the hexene yield decreases and the hexene scavenging the hydrogen atom becomes a hexyl radical:

$$C_6H_{12} + H \longrightarrow C_6H_{13} \qquad (22)$$

Consequently, the yield of hexyl radicals would not change whether reaction (13) or reaction (22) occurs. On the other hand, the dodecanes are probably produced only by reaction (21). Therefore, the dodecane yields do not change with an increase in the dose, while the hexene yields decrease with such an increase.

iii) Effects of C_2H_5OH and NO. As is shown in Fig. 3 and Table 5, the *G*-values of the radiolysis products in the presence of C_2H_5OH are similar to the case of NH_3. Since the ionization potential of C_2H_5OH (IP=10.50 eV)[14] is a little higher than that of *n*-hexane (IP=10.17 eV),[15] the charge-transfer reaction, if any, from a parent *n*-hexane ion to C_2H_5OH can be ignored. As C_2H_5OH has a comparatively high proton affinity (PA=8.39 eV),[38] the proton-transfer reaction from a parent *n*-hexane ion to C_2H_5OH is most probable. On the other hand, the reaction of C_2H_5OH with electrons and radicals is probably unimportant under the present conditions in view of the reactivity of these reactive species and the concentration of C_2H_5OH. Therefore, the proton-scavenging effect of C_2H_5OH shown by Buchanan *et al.*[10] in the case of cyclohexane appears to have an effect similar to that of the addition of NH_3. The proton-scavenging reaction and the subsequent neutralization reaction are shown by the following schemes:

$$n\text{-}C_6H_{14}^+ + C_2H_5OH \longrightarrow C_6H_{13} + C_2H_5OH_2^+ \qquad (23)$$

$$C_2H_5OH_2^+ + e^- \longrightarrow C_2H_5OH + H \qquad (24)$$

The results with added NO are shown in Fig. 8 and Table 5. Since the *G*-values of hexenes in the presence of NO are much less than those with added SO_2, whose main effect is concluded to be radical scavenging, the added NO apparently undergoes reactions other than radical scavenging. Though the details of the effect other than radical scavenging can not be clarified in this work, it may be concluded that NO can not be used as a simple radical scavenger.

iv) Formation of the $C_6H_{13}^+$ Ion. The results obtained in the coexistence of SF_6 and NH_3 are shown in Tables 3 and 4. Since the results are somewhat singular, a re-examination of the radiolysis mechanism described in the previous section is necessary. The results show that, when SF_6 and NH_3 are both present, the total *G*-value of the hexenes increases more than one unit from the value obtained in the presence of SF_6 only, but that the other product yields are nearly equal to the values obtained in the presence of SF_6 only. In the coexistence of SF_6 and NH_3, it can be assumed that reactions (1) and (3) and the subsequent neutralization reaction (25) occur:

$$NH_4^+ + SF_6^- \longrightarrow NH_4F + SF_5 \qquad (25)$$

The evidence for reaction (25) is as follows. The reaction (25) is calculated to be exothermic by *ca.* 7 eV. In the coexistence of SF_6 and NH_3, an insoluble product was found in *n*-hexane. The product dissolved easily in water, and the resultant aqueous solution showed the existence of F^- and NH_4^+ ions when alizarin complexone[39] and Nessler's reagent were used respectively. If, in the radiolysis mechanism of *n*-hexane assumed before, the SF_5 produced from reaction (25) caused the *G*-value of the total hexene to increase by 1.44, as is shown in Table 3, and if it simultaneously made the *G*-values of other products to remain almost at the values obtained by the addition of SF_6 only, the following two reactions, (26) and (27) would have also to be assumed and, further, all the hexyl radicals produced from reaction (3) would have to carry out these reactions:

$$SF_5 + C_6H_{13} \begin{cases} \nearrow SF_5H + C_6H_{12} & (26) \\ \searrow SF_5C_6H_{13} & (27) \end{cases}$$

However, it is unreasonable to consider that all the hexyl radicals produced from reaction (3) undergo only reaction (26) and (27), for reactions (20), (21), and (28) could also be considered.

$$SF_5 + SF_5 \longrightarrow S_2F_{10} \qquad (28)$$

Consequently, the formation of the $C_6H_{13}^+$ ion during irradiation could be suggested as explaining the results obtained in the coexistence of NH_3 and SF_6. If the fragment ions had been produced according to the pattern of the mass-spectra of *n*-hexane[40] in such a large yield as to correspond to the required yield of $C_6H_{13}^+$ ions, the yield of fragment paraffin products would have been larger than that of the congruent fragment olefin products; *e. g.*, the yield of C_3H_8 would have been larger than that of C_3H_6 in the presence of a radical scavenger because of an H^--transfer reaction from *n*-hexane to a fragment ion. However, such a result could not be obtained, as is shown in Table 3 (column: SO_2). Therefore, H^--transfer reaction from *n*-

---

[37] H. A. Dewhurst, *J. Phys. Chem.*, **63**, 813 (1959).

[38] V. L. Tal'rose and E. L. Frankevitch, *J. Amer. Chem. Soc.*, **80**, 2344 (1958).

[39] H. Hashitani, H. Yoshida and H. Muto, *Bunseki Kagaku*, **16**, 44 (1967).

[40] L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.*, **30**, 1605 (1959).

hexane to fragment ions, *e. g.*, the $C_3H_7^+$ ion, does not appear to play an important role in the formation of the $C_6H_{13}^+$ ion; the $C_6H_{13}^+$ ion can be thus tentatively assumed to be produced by the direct excitation shown by reaction (29):

$$n\text{-}C_6H_{14} \longrightarrow C_6H_{13}^+ + H + e^- \quad (29)$$

In the case of the addition of SF_6, an additional reaction, (30), may be assumed to occur besides reactions (1) and (2), and in the case of addition of NH_3, an additional reaction, (31), may be assumed to occur besides reactions (3) and (4). The SF_5 produced by reaction (25) probably undergoes reactions (26), (27) and (28).

$$C_6H_{13}^+ + SF_6^- \longrightarrow C_6H_{13} + SF_6 \quad (30)$$

$$C_6H_{13}^+ + NH_3 \longrightarrow C_6H_{12} + NH_4^+ \quad (31)$$

Assuming such a radiolysis mechanism including the existence of the $C_6H_{13}^+$ ion as has been described above, the increase in the hexene yield in the presence of both SF_6 and NH_3 from the value obtained in the presence of SF_6 only would be due to reactions (26) and (31), and the result that the G-values of all the products except for hexenes in the presence of both SF_6 and NH_3 are almost the same as in the case of the addition of SF_6 only is qualitatively explicable by the inferences that a part of the hexyl radicals produced by reaction (3) escapes reactions (26) and (27), and that the escaping amount is almost equal to the amount produced by reaction (30) in the presence of SF_6 only. As there seem to be no data on the reactivity of SF_5 except that Ingen *et al.*[41] have recently suggested that SF_5 does not abstract an H atom from cyclohexane, the G-value of the $C_6H_{13}^+$ ion can not be accurately estimated. However, it must be less than 1.26, which is the total hexene yield obtained in the presence of SO_2. Further investigation is necessary to confirm that the assumption of the existence of the $C_6H_{13}^+$ ion in the liquid phase is appropriate, for it seems to difficult for such a direct fragmentation as is shown by reaction (29) to occur in the gas phase.[40]

v) The *G*-value of Ionization. Considering the radiolysis mechanism and the effect of added SF_6 described before, the decrease in the G-value of the decomposition of n-hexane upon the addition of SF_6 from that obtained without additives can be approximately regarded as the G-value of the ionization of n-hexane in the liquid phase. The G-value of the decomposition of n-hexane can be obtained by adding the G-value of hexyl radicals which react with other radicals to give a n-hexane molecule by disproportionation to the G-value of the net decomposition of n-hexane. The G-value of net decomposition in the presence of SF_6 is obtained in the same manner, as is shown by Eqs. (A) and (B), except that the G-value obtained in the presence of SF_6 is used instead of that obtained without additives; this value was calculated to be 4.16 from Tables 3 and 4. The G-value of hexyl radicals which react with other radicals to give a n-hexane molecule by disproportionation is not included in the above G-value of the net decomposition; it can be approximately calculated by using the G-value of the total dodecanes and the ratio of k_d to k_c, k_d/k_c, where k_d and k_c indicate the average rate constants of the disproportionation reaction and the combination reaction between hexyl radicals respectively. To be exact, there are three kinds of hexyl radicals produced by irradiation, and the ratio of the rate constants of the disproportionation reaction to that of the combination reaction between these radicals seems to be dependent on the combination of these three kinds of radicals. In this work, however, the average rate constants, k_d and k_c, were used as approximate values. Considering the radiolysis mechanism and the effect of added SO_2 described above, the k_d/k_c ratio can be approximately expressed by the following equation, (C):

$$k_d/k_c = \{G_0(C_6H_{12}) - G_1(C_6H_{12}) - \Delta G\}/G_0(C_{12}H_{26}) \quad (C)$$

where $G_0(C_6H_{12})$ and $G_0(C_{12}H_{26})$ indicate the total hexene yield and the total dodecane yield in the absence of additives respectively, where $G_1(C_6H_{12})$ indicates the total hexene yield in the presence of SO_2, and where ΔG indicates the hexene yield formed by reaction (17) in the absence of additives. ΔG was calculated by using the radical yields obtained by Holroyd[42] and the G-values of the C_7-C_{10} products shown in Table 2 on the assumptions that the ratio of the rate constants of the disproportionation reactions, (17) and (18), to the combination reaction, (19), is 0.25 and that the rate constant of reaction (17) is equal to that of reaction (18). Thus, ΔG was calculated to be about 0.09. By substituting the values of $G_0(C_6H_{12})$, $G_0(C_{12}H_{26})$, and $G_1(C_6H_{12})$ shown in Tables 3 and 4, and ΔG for Eq. (C), k_d/k_c was estimated to be 1.33. Consequently, the decomposition yield in the presence of SF_6 was calculated to be 5.05 by adding the G-value of the disproportionation reaction of the hexyl radical, 0.89, to the G-value of the net decomposition, 4.16. On the other hand, the decomposition yield in the absence of additives was calculated to be 9.02 in the same manner. The difference, 3.97, can be regarded as the G-value by which the decomposition of n-hexane is suppressed by the added SF_6; it may also be regarded as approximately the G-value of the ionization of n-hexane in the liquid phase. This value is a little smaller than the value, 4.27, obtained by using the

---

[41] J. W. F. van Ingen and W. A. Cramer, *J. Phys. Chem.*, **74**, 1134 (1970).

[42] R. A. Holroyd, "Aspects of Hydrocarbon Radiolysis," ed. by T. Gäumann and J. Hoigné, Academic Press, New York, N. Y. (1968), p. 13.

W-value[43] of *n*-hexane in the gas phase, but it is close to the corresponding value, 3.9, obtained for liquid cyclohexane by Warman *et al.*[44]

vi) G(N_2) in the Presence of N_2O. In the presence of N_2O, the following reaction, (32), which shows the electron - scavenging effect of N_2O, is well known[8,45,46] as one of the processes which bring about nitrogen:

$$e^- + N_2O \longrightarrow N_2 + O^- \quad (32)$$

Though reaction (33) also produces nitrogen, this reaction may be ruled out because the rate constant of this reaction is relatively small, *i.e.*, $k = 1.2 \times 10^4 \text{M}^{-1}\ \text{sec}^{-1}$ at 150°C.[47]

$$H + N_2O \xrightarrow{k} HO + N_2 \quad (33)$$

As another reaction producing nitrogen, Holroyd[48] has suggested the following reaction, (34), which includes the decomposition of N_2O by excitation transfer from the excited *n*-hexane to N_2O:

$$n\text{-}C_6H_{14}^* + N_2O \longrightarrow n\text{-}C_6H_{14} + N_2 + O \quad (34)$$

Though the formation of nitrogen as a result of a subsequent reaction of O^- ion with N_2O can not be excluded completely, such a reaction to form nitrogen may tentatively be assumed to be negligible compared with the reaction of the O^- ion with *n*-hexane because the latter reaction seems to be quite fast (the rate constant of hydrogen - atom abstraction reaction from $n\text{-}C_4H_{10}$ by the O^- ion has been reported to be $7.2 \times 10^{11} \text{M}^{-1}\ \text{sec}^{-1}$ in the gas phase).[49] By using the *G*-value of ionization obtained in the previous section, the $G(N_2)$ evolving from reaction (32) may be 3.97 at most. On the other hand, as may be seen in Fig. 6, $G(N_2)$ in the presence of N_2O shows little increase at a concentration of about 0.5M and the *G*-value at 0.5M of N_2O was 5.29. At least, the difference in these *G*-values, 1.32, may be attributed to a reaction other than reaction (32). Assuming that reaction (34) is responsible for this difference, and that the O^- ion and the oxygen atom produced by reactions (32) and (34) respectively subsequently undergo the following reactions, (35) to (39), water should be observed at the same *G*-value as that of nitrogen, and the decomposition yield of *n*-hexane in the presence of N_2O should increase by at least the *G*-value, 2.64, which is calculated to be twice as much as the *G*-value of reaction (34):

$$O^- + n\text{-}C_6H_{14} \longrightarrow OH^- + C_6H_{13} \quad (35)$$

$$OH^- + n\text{-}C_6H_{14}^+ \longrightarrow H_2O + C_6H_{13} \quad (36)$$

$$OH^- + C_6H_{13}^+ \longrightarrow H_2O + C_6H_{12} \quad (37)$$

$$O + n\text{-}C_6H_{14} \longrightarrow OH + C_6H_{13} \quad (38)$$

$$OH + n\text{-}C_6H_{14} \longrightarrow H_2O + C_6H_{13} \quad (39)$$

Gäumann *et al.*[5,7] have reported that, in the same system as was studied in this work, *i.e.*, an *n*-hexane solution of N_2O, hexanol could not be observed as a product, but that water was observed in yield of 3.2±0.8 at the N_2O concentration of 0.06M. This *G*-value of water is approximately equal to the *G*-value of nitrogen, 3.35, as may be seen in Fig. 6. This is not inconsistent with the reaction mechanism discussed above in terms of the yield of nitrogen. On the other hand, the decomposition yield of *n*-hexane in the presence of N_2O was calculated to be 11.28 by using the product yields shown in Tables 3 and 4 and the value of k_d/k_c in the manner described earlier. Since the decomposition yield of *n*-hexane in the absence of additives is 9.02, the difference in these values, 2.26, may be regarded as the *G*-value by which the decomposition of *n*-hexane is promoted by the addition of N_2O. This value is close to the value, 2.64, mentioned earlier. This result seems to support the reaction mechanism supposed earlier in regard to the yield of nitrogen. For the purpose of clarifying further the mechanism for producing nitrogen, however, it is necessary to measure more accurately the yields of water and other oxygenated products.

The authors wish to express their thanks to Dr. S. Sato, Dr. H. Yamazaki and Dr. Y. Hatano of this institute and Dr. T. Miyazaki of Nagoya University for their helpful suggestions. They also wish to thank Miss H. Yamaguchi for assistance in preparing the manuscript.

---

43) P. Adler and H. K. Bothe, *Z. Naturforsch.*, **20a**, 1700 (1965).

44) J. M. Warman, K.-D. Asmus and R. H. Schuler, *J. Phys. Chem.*, **73**, 931 (1969).

45) S. Sato, R. Yugeta, K. Shinsaka and T. Terao, This Bulletin, **39**, 156 (1966).

46) G. J. Schulz, *J. Chem. Phys.*, **34**, 1788 (1961).

47) M. Schiavello and G. G. Volpi, *ibid.*, **37**, 1510 (1962).

48) R. A. Holroyd, *J. Phys. Chem.*, **72**, 759 (1968).

49) D. K. Bohme and F. C. Fehsenfeld, *Can. J. Chem.* **47**, 2717 (1969).