BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3400—3404 (1970)

The Effect of Chloromethanes on Hydrogen Formation in the Radiolysis of Methylcyclohexane and 3-Methylpentane at −196°C

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(Received June 4, 1970)

The effect of chloromethanes (CH_2Cl_2, $CHCl_3$ and CCl_4) on hydrogen formation from γ-irradiated methylcyclohexane (MCH) and 3-methylpentane (3MP) at −196°C was investigated. It was found that the decrease in hydrogen yield by the presence of CH_2Cl_2 was almost the same as that caused by an electron scavenger such as N_2O, *n*-butyl chloride, SF_6 or iodobenzene, but the hydrogen yield was much lower in the presence of $CHCl_3$ or CCl_4 than other electron scavengers. Although the yield of $CCl_3\cdot$ radicals formed from dissociative electron attachment to CCl_4 in CCl_4-MCH systems was $\sim$1.4 *G*, the decrease in hydrogen yield was $\sim$3 *G*. A similar result was obtained for $CHCl_3$-MCH systems. Thus we have ascribed the effect of CH_2Cl_2 on hydrogen formation to electron scavenging and that of $CHCl_3$ or CCl_4 to excitation transfer as well as electron scavenging. ESR studies on radical formation from these systems also support the above interpretation.

It is not easy to determine the role of excited molecules in radiolysis. Energy transfer from cyclohexane to benzene, originally proposed by Manion and Burton,[1] does not seem to be excitation transfer, but positive charge transfer in the light of recent studies.[2-7] Though excitation transfer was proposed for quenching of fluorescence from a γ-irradiated cyclohexane system,[8] some ionic process was recently suggested for this phenomenon.[4-7] A study which clearly demonstrated excitation transfer was that by Collinson *et al.*,[9] who found a sudden increase in the reduction yield of $FeCl_3$ in benzene when the temperature of the system was lowered below the melting point and ascribed it to excitation transfer.

We have shown in a previous work[10] that carbon tetrachloride lowers the yields of hydrogen and of solvent radicals from γ-irradiated methylcyclohexane (MCH) at −196°C much more than electron scavengers, such as SF_6 or N_2O, and ascribed the effect of carbon tetrachloride to excitation transfer as well as electron scavenging. We have extended the previous study of CCl_4 in MCH to other chloromethanes ($CHCl_3$ and CH_2Cl_2) in order to investigate their effects on the hydrogen yield from MCH γ-irradiated at −196°C. We also examine the effect of these chloromethanes on the radiolysis of 3-methylpentane (3MP) systems. In order to examine the possibility of excitation transfer from 3MP to chloromethanes, it was necessary to investigate the effect of electron scavengers on hydrogen yields from 3MP. Though 3MP has been widely used as a matrix for measurements of reaction intermediates, only a few studies on hydrogen formation have been reported.[11,12] Thus we attempted to investigate the effect of N_2O as an electron scavenger on the hydrogen formation from γ-irradiated 3MP.

Experimental

Materials. MCH was Tokyo Kagaku Seiki 99.9% and used as received. Aldrich 3MP was shaken with concentrated sulfuric acid in a separating flask, washed with distilled water, and then dried over sodium sulfate. After passing through a silica gel column, 3MP was fractionally distilled before use. Carbon tetrachloride, chloroform and methylene dichloride were

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

2) W. V. Dusen and W. H. Hamill, *J. Amer. Chem. Soc.*, **84**, 3648 (1962).

3) S. Z. Toma and W. H. Hamill, *ibid.*, **86**, 1478 (1964).

4) M. Burton, *Mol. Cryst.*, **4**, 61 (1968).

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

9) E. Collinson, J. J. Conlay and F. S. Dainton, *Discuss. Faraday Soc.*, **1963**, 1531.

10) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, This Bulletin, **43**, 1017 (1970).

11) M. G. Robinson and G. R. Freeman, *J. Chem. Phys.*, **48**, 983 (1968).

12) T. Kimura, K. Fueki and Z. Kuri, This Bulletin, **43**, 1657 (1970).

Nakarai Kagaku specially prepared reagent and used as received. N_2O was Takachiho Shoji Co. 99.9% and used as received.

Sample preparation. Amounts of liquid materials were measured volumetrically. Usually 1 m*l* of MCH or 3MP was used for a sample. Solutions in irradiation cells equipped with a break-seal (usually 2 m*l*) were degassed by the freeze-pump-thaw technique and then sealed off. N_2O was introduced into a bulb of known volume to the desired pressure and then condensed into the irradiation cell.

Irradiation. A 3000 Ci ^{60}Co source was used for γ-irradiation. Irradiation doses were 2.51×10^{20} eV/g at 20°C, 1.97×10^{20} eV/g at -72°C and 2.23×10^{20} eV/g at -196°C.

Analysis. Gaseous products noncondensable at liquid nitrogen temperature were collected by a Toepler pump and their quantities were determined by the PVT method. To convert hydrogen into water, the gas was circulated about 20 times through a cupric oxide furnace, heated at 220—260°C, and a liquid nitrogen trap, and then the residual gas was recollected and its quantity was measured. Yields of solvent and solute radicals were determined by ESR technique in the same manner as reported[10] previously.

Results and Discussion

Figures 1, 2 and 3 show the effect of N_2O on hydrogen formation from γ-irradiated 3MP at 20°C, -72°C and -196°C, respectively. The decrement of hydrogen yield with increasing N_2O concentration at -196°C is lower than at 20°C and -72°C, while the nitrogen yield at 20°C is somewhat lower than those at -72°C and -196°C. It has been proposed that the nitrogen yield is twice the yield of scavenged electrons in the radiolysis of cyclohexane at room temperature.[13] It can be seen from Fig. 1 that the ratio of the nitrogen yield to the decrease in hydrogen yield is about 3 in N_2O-3MP systems at 20°C. The difference in the ratio, $G(N_2)/\Delta G(H_2)$, between cyclohexane and 3MP may be explained in terms of the difference in the decomposition pattern between branched and non-branched hydrocarbons[12]; a part of energy which is consumed in C–H bond cleavage in the case of non-branching hydrocarbons is spent for C–C bond cleavage in the case of branching hydrocarbons. Recently Asmus *et al.* have suggested that the efficiency of hydrogen formation from ion recombination is 0.6 in the case of 3MP.[14] With this value, the yield of electrons scavenged by N_2O at 20°C is given by $(1/0.6)\Delta G(H_2)$. Thus the ratio of the nitrogen yield to the yield of scavenged electrons is $G(N_2)/\{(1/0.6)\Delta G(H_2)\}=\sim2$. Such

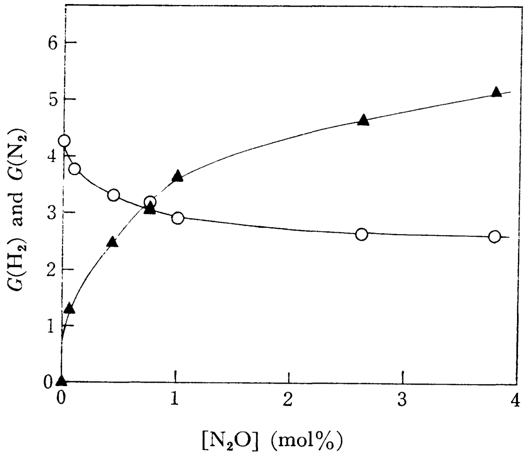

Fig. 1. Yields of hydrogen and nitrogen from γ-irrddiated N_2O-3MP systems at 20°C.
○; $G(H_2)$, ▲; $G(N_2)$

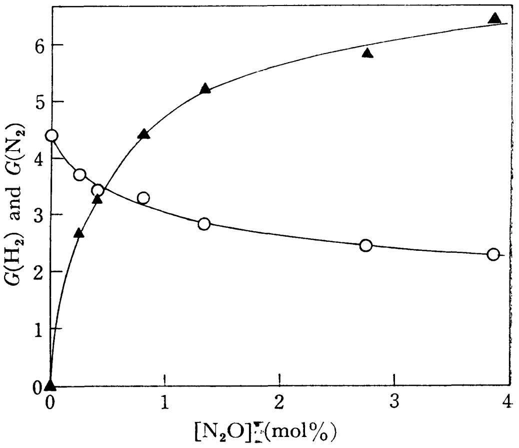

Fig. 2. Yields of hydrogen and nitrogen from γ-irradiated N_2O-3MP systems at -72°C.
○; $G(H_2)$, ▲; $G(N_2)$

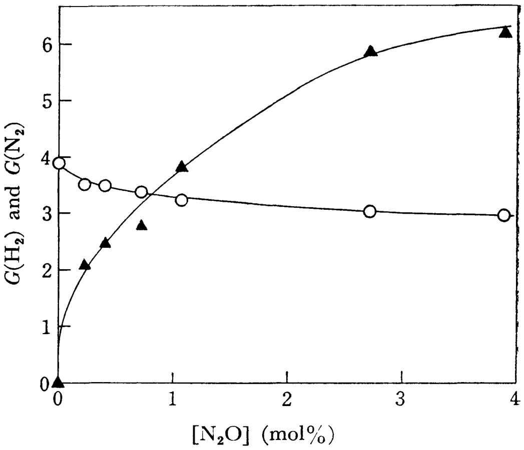

Fig. 3. Yields of hydrogen and nitrogen from γ-irradiated N_2O-3MP systems at -196°C.
○; $G(H_2)$, ▲; $G(N_2)$

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[13] S. Sato, R. Yugeta, K. Shinsaka and T. Terao, *ibid.*, **39**, 156 (1966).

[14] K. D. Asmus, J. M. Warman and R. H. Schuler, *J. Phys. Chem.*, **74**, 246 (1970).

argument may be applied to the case of N_2O-3MP systems at $-72°C$, although the nitrogen yield at $-72°C$ is slightly higher than that at 20°C. The nitrogen yield at $-196°C$ is almost the same as that at 20°C and $-72°C$, but we do not think that the yields of scavenged electrons in these three cases are the same. We have shown that the ratio of the nitrogen yield to the decrease in hydrogen yield in N_2O-MCH systems γ-irradiated at $-196°C$ depends upon the N_2O concentration and it increases from 1 to 4 with increasing N_2O concentration, and that the neutralization of an MCH positive ion with an electron leads to the formation of one hydrogen molecule.[15] Our result in which the efficiency of hydrogen formation from ion recombination is ~ 1 is in rough agreement with that by Asmus *et al.*[14] Thus we have estimated the ratio of the nitrogen yield to the yield of electrons scavenged by N_2O in N_2O-MCH systems at $-196°C$ ~ 4 at higher N_2O concentrations. Using the result by Asmus *et al.*,[14] the ratio of the nitrogen yield to the yield of scavenged electrons, $G(N_2)/G(e^-)$, in 3MP at $-196°C$ is $G(N_2)/\{(1/0.6)\cdot \Delta G(H_2)\} = \sim 4$. The process of nitrogen formation other than Eq. (1) is not clear, but the relation $G(N_2)/G(e^-) = \sim 4$ holds for 3MP as well as MCH at $-196°C$.

$$N_2O + e^- \longrightarrow N_2O^- \longrightarrow N_2 + O^- \qquad (1)$$

The mechanism of nitrogen formation other than Eq. (1) may be short chain reactions,[16] excitation transfer[17] or negative charge transfer from O^- to N_2O.[15] Considering the relation $G(N_2)/G(e^-) = \sim 4$ in 3MP and MCH, it seems that nitrogen is formed via negative ion processes such as Eq. (1). Assuming that $G(N_2)/G(e^-)$ is 4 in 3MP at $-196°C$, $G(e^-)$ is estimated to be 1.57 at the highest N_2O concentration studied, which is considerably lower than that at 20°C. Such a low yield of scavenged electrons in 3MP at $-196°C$ has been reported by us.[18] Therefore we can say that the hydrogen yield and the yield of scavenged electrons at $-196°C$ are lower than those at 20°C in the case of 3MP as well as MCH.

Hydrogen yields from γ-irradiated MCH and 3MP at $-196°C$ in the presence of CH_2Cl_2, $CHCl_3$ or CCl_4 are shown in Figs. 4 and 5, respectively. The yield of hydrogen was calculated using the following equation:[*1]

$$G(H_2) = \frac{P - G'(H_2)\cdot D'\cdot W_s}{D\cdot W} \qquad (I)$$

where P is the number of hydrogen molecules produced, $G'(H_2)$ is the yield of hydrogen from pure solute, D and D' are the doses absorbed by solvent of unit weight and that by solute of unit weight, respectively, and W and W_s are the weights of solvent and solute, respectively. The values of $G'(H_2)$ were 0.186 for CH_2Cl_2 and 0.109 for $CHCl_3$. Although the solubility of CH_2Cl_2 at $-196°C$ is poor compared with that of $CHCl_3$ or CCl_4, solutions of CH_2Cl_2 in MCH form a transparent glass in the concentration range below 3 mol%. The dashed lines in Figs. 4 and 5 indicate that the solutes are not adequately soluble. The decrement of the hydrogen yield from CH_2Cl_2-MCH systems in Fig. 4 agrees well with that from N_2O-MCH

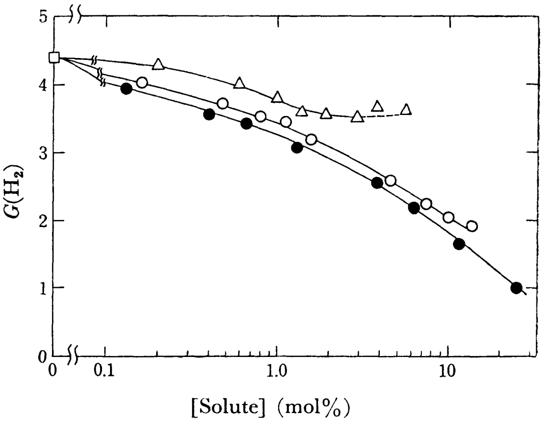

Fig. 4. Yields of hydrogen from γ-irradiated pure MCH (□), MCH in the presence of CH_2Cl_2 (△), $CHCl_3$ (○) and CCl_4 (●) at $-196°C$.

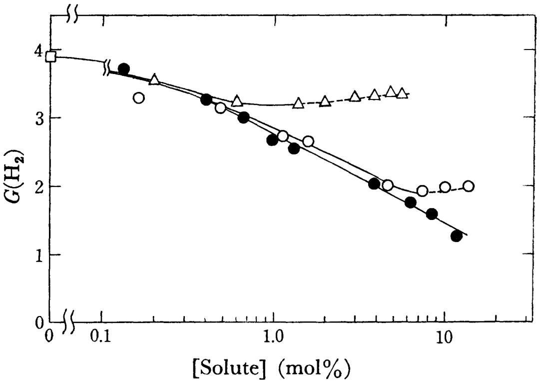

Fig. 5. Yields of hydrogen from γ-irradiated pure 3MP (□), 3MP in the presence of CH_2Cl_2 (△), $CHCl_3$ (○) and CCl_4 (●) at $-196°C$.

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[15] T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, This Bulletin, **41**, 2861 (1968).

[16] W. J. Holtslander and G. R. Freeman, *Can. J. Chem.*, **45**, 1649 (1967).

[17] R. A. Holroyd, *J. Phys. Chem.*, **72**, 759 (1968).

[18] T. Kimura, K. Fueki and Z. Kuri, presented at 23rd Annual Meeting of the Chemical Society of Japan, April, 1970, Tokyo; This Bulletin, **43**, 3090 (1970).

[*1] The G value usually employed in a binary system (A-B), *viz.*, the number of product molecules per 100 eV of the energy absorbed by both A and B, is useful only for knowing whether there is an interaction between A and B. The merit of Eq. (I) is that we can see the extent of the interaction; if there is no interaction, G value from Eq. (I) is constant but if there is an interaction it varies corresponding to the extent of the interaction.

systems.[15] Thus the effect of CH_2Cl_2 on the hydrogen formation can be regarded as the same as that of an electron scavenger such as N_2O or SF_6. However, both $CHCl_3$ and CCl_4 suppress the hydrogen formation much more than CH_2Cl_2. The effects of these chloromethanes in 3MP (Fig. 5) are similar to that for MCH.

We now examine the reason for the abnormal suppression of hydrogen formation by $CHCl_3$ or CCl_4. We previously suggested the possibility of excitation transfer.[10] It was shown that H atoms abstract chlorine atoms from $CHCl_3$ or CCl_4 in cyclohexane at room temperature.[19,20] Further, Teplý and Janovský reported the suppression of hydrogen formation by CCl_4 in γ-irradiated glassy methanol at $-196°C$ and ascribed it to Cl atom abstraction from CCl_4 by H atoms in addition to the suppression of charge neutralization.[21] However, Stone denied Cl atom abstraction by H atoms at $-196°C$.[22] We have shown that the hydrogen yields from thermal H atoms at $-196°C$ are 0.5 *G* in MCH and 0.65 *G* in 3MP.[12] Thus, the decrements of hydrogen yield from MCH and 3MP at $-196°C$ in Figs. 4 and 5 cannot be explained only by Cl atom abstraction by thermal H atoms.

The abnormal suppression of hydrogen yield by $CHCl_3$ or CCl_4 is explicable if the yield of electrons scavenged by $CHCl_3$ or CCl_4 is higher than that by other electron scavengers. If this is true, the yield of scavenged electrons in MCH should be ~3 *G* at the highest CCl_4 concentration studied because the decrement of the hydrogen yield is ~3 *G*. Thus, the yield of $CCl_3\cdot$ radicals in MCH produced by Reaction (2) is expected to be ~3 *G*. For the sake of confirmation, we attempted to determine the yields of $CCl_3\cdot$ radicals in MCH by ESR and the results are shown in Fig. 6. The yield of $CCl_3\cdot$ radicals in MCH increases with increasing CCl_4 concentration and reaches a constant value at CCl_4 concentrations above 2 mol %. The experimental curve for the yield of $CHCl_2\cdot$ radicals produced by Reaction (3) was very similar to that for $CCl_3\cdot$ radicals although the former was somewhat lower in the lower solute concentration range.

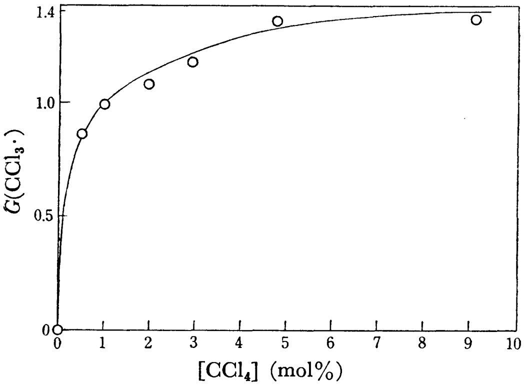

Fig. 6. Yields of $CCl_3\cdot$ radicals from γ-irradiated CCl_4-MCH systems at $-196°C$.

$$CCl_4 + e^- \longrightarrow CCl_3\cdot + Cl^- \qquad (2)$$

$$CHCl_3 + e^- \longrightarrow CHCl_2\cdot + Cl^- \qquad (3)$$

The limiting value of $CCl_3\cdot$ radicals in Fig. 6 is 1.4 *G* which agrees well with the yield of scavenged electrons in MCH glass obtained by the different procedures.[18,23] Thus the yield of $CCl_3\cdot$ radicals produced from Cl atom abstraction by H atoms seems to be very low, if produced at all. We are inclined to ascribe the abnormal suppression of hydrogen yield by $CHCl_3$ or CCl_4 to the excitation transfer from excited solvent molecules to solutes.

Another support for the excitation transfer mechanism was obtained from ESR experiments. We determined the yields of MCH· radicals in γ-irradiated MCH glasses containing CH_2Cl_2, $CHCl_3$ or CCl_4. The results are shown in Fig. 6.

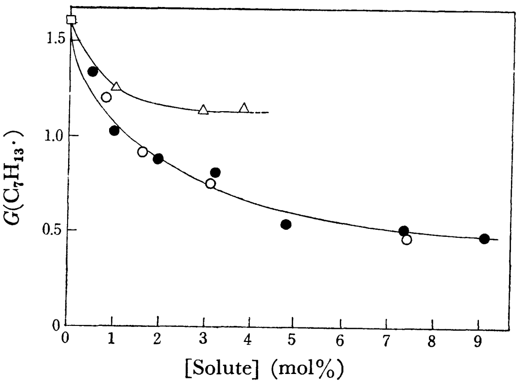

Fig. 7. Yields of MCH· radicals from γ-irradiated pure MCH (□) containing CH_2Cl_2 (△), $CHCl_3$ (○) and CCl_4 (●) at $-196°C$.

In a previous work we have shown that electron scavengers such as SF_6 or *n*-butyl chloride suppress the formation of MCH· radicals by ~25% at a solute concentration of about 5 mol%.[10] This implies that the suppression of neutralization of solvent positive ions with electrons leads to the decreases in solvent radical yield of about 25%. Thus, the origin of solvent radicals seems to be mainly the decomposition of directly excited molecules and only partly the neutralization of positive

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21) J. Teplý and I. Janovský, *Int. J. radiat. Phys. Chem.*, **1**, 117 (1969).

22) J. A. Stone, *Can. J. Chem.*, **46**, 1267 (1968).

23) T. Shida and M. Imamura, presented at 23rd Annual Meeting of the Chemical Society of Japan, April, 1970, Tokyo.

ions with electrons. Since the decrement of MCH· radical yield by the addition of CH_2Cl_2 is nearly equal to that by SF_6 or *n*-butyl chloride,[10] the effect of CH_2Cl_2 on radical formation can be ascribed to electron scavenging, which is consistent with the result on hydrogen formation. We can see from Fig. 7 that both $CHCl_3$ and CCl_4 suppress the formation of solvent radicals to a greater extent than CH_2Cl_2. Thus, we can ascribe the effect of $CHCl_3$ or CCl_4 on the radical formation to excitation transfer in addition to electron scavenging.

If we exclude the role of excitation transfer for the abnormal suppression of the yields of hydrogen and solvent radicals, the only possible cause for this will be electron scavenging by $CHCl_3$ and CCl_4 which is nondissociative.

$$CHCl_3 + e^- \longrightarrow CHCl_3^- \qquad (4)$$

$$CCl_4 + e^- \longrightarrow CCl_4^- \qquad (5)$$

Suppression of radical formation by these solutes can be explained by Reactions (4) and (5), if radicals are mainly formed by neutralization of positive ions with electrons. At present, however, we have no evidence for nondissociative electron capture by these solutes in condensed systems. Thus it appears reasonable to ascribe the abnormal suppression of hydrogen and radical formation by $CHCl_3$ or CCl_4 to excitation transfer.