BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 934—937 (1971)

Effect of Phase on Excitation Transfer in the Radiolysis of Isobutane

Tetsuo MIYAZAKI, Takahisa YAMADA, Terunobu WAKAYAMA, Kenji FUEKI, and Zen-ichiro KURI
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

(Received September 10, 1970)

The effects of CCl_4 on the formation of H_2 and C_4H_9 radicals in the radiolysis of i-C_4H_{10} have been studied in glass at 77°K and the liquid at 195°K. The yield of H_2, which is not affected by the addition of N_2O or SF_6, decreases sharply upon the addition of CCl_4 in the glass, as in the crystal (This Bulletin, **42**, 1164 (1969); **43**, 1017 (1970).), while it does not so sharply decrease in the liquid as in the solid. The effects of CCl_4 on the yields of H_2 correspond fairly well to those on the yields of the C_4H_9 radicals. The effects of CCl_4 in the glass are explained by the excitation transfer from the excited butane molecule to CCl_4, as in the radiolysis of i-C_4H_{10} in the crystal. A kinetic treatment suggests that its mechanism may be the exciton transfer. Some remarks on the primary process of ionization in the radiolysis of solid hydrocarbons are given from the viewpoint of exciton transfer.

We have studied the radiolysis of isobutane in the crystalline state at 77°K by ESR spectroscopy and product analysis. Though the yields of C_4H_9 radicals and hydrogen do not decrease in the presence of conventional electron scavengers, they decrease remarkably upon the addition of CCl_4.[1] The characteristic effects of CCl_4 have been ascribed to exciton transfer from a kinetic consideration. Recently it has been found that the radiolysis of solid isobutane is affected appreciably by its state, by whether it is glass or polycrystal.[2] Although the isobutyl radical is formed in the crystalline state by γ-irradiation, the t-C_4H_9 radical is formed in the glassy state. The yields of CH_4 and C_3H_6 in the radiolysis of solid isobutane are much higher in the polycrystalline state than in the glassy state. It has been suggested that a plausible explanation of the phase effect is in terms of the difference between the efficiency of energy transfer in the glass and that in the polycrystal.

Here we have studied the effects of the phase on the excitation transfer to CCl_4 in the radiolysis of isobutane.

Experimental

The isobutane, methylcyclohexane (MCH), nitrous oxide, and carbon tetrachloride were all the same as those which had been used before.[1,2] The sulfur hexafluoride (Matheson Co.) was of a high purity. The samples were irradiated with Co-60 γ-rays at a dose rate of 4.2×10^5 rad/hr. The ESR measurements were made on a JES-3BX ESR spectrometer. The gaseous products not condensable at the temperature of liquid nitrogen were analyzed by a gas burette connected to a Toepler pump and a copper oxide furnace kept at 240°C.

Pure isobutane forms a polycrystalline solid at 77°K. When a sample of isobutane containing a small amount of MCH is plunged into liquid nitrogen, it forms a clear glass. The concentration of MCH in the radiolysis of glass for the product analysis is different from that for the ESR measurement. This is because the state of the glass depends upon the concentration of MCH. The glass at a high concentration of MCH is unfavourable for the detection of radicals by ESR, because the matrix is so soft that the radicals are not trapped. Therefore, the concentration of MCH chosen for the measurement of the C_4H_9 radical is 4 mol/100 mol of i-C_4H_{10}. The glass at a low concentration of MCH is, however, so unstable that it becomes crystalline during a long γ-irradiation time. Therefore, when the yield of H_2 is measured in the radiolysis in the glassy state, the chosen concentration of MCH is 10 mol/100 mol of i-C_4H_{10}.

Results

Formation of Hydrogen. In the radiolysis of i-C_4H_{10}-MCH(10 mol/100 mol of i-C_4H_{10}) system, N_2O and SF_6 are added in the glassy state in order to suppress the formation of hydrogen by a neutralization reaction (reactions (1) and (2)), if any should occur:

$$C_4H_{10} \rightsquigarrow C_4H_{10}^+ + e^- \tag{1}$$

$$C_4H_{10}^+ + e^- \rightarrow H,\ H_2,\ P \tag{2}$$

where P represents some radicals or molecules. As is shown in Table 1, the yield of hydrogen does not decrease at all upon the addition of electron scavengers, such as N_2O and SF_6. Since $G(N_2)$ amounts to 1.4—1.6 in the radiolysis of i-C_4H_{10}-MCH(10 mol/100 mol of the i-C_4H_{10})-N_2O(3 mol/100 mol of i-C_4H_{10}) system, N_2O captures electrons efficiently to produce N_2, as

TABLE 1. RADIOLYSIS OF i-C_4H_{10}—MCH($10^{a)}$) SYSTEM IN THE GLASSY STATE AT 77°K
TOTAL DOSE: 4.3×10^6 RAD

	$G(H_2)$	$G(CH_4)$	$G(N_2)$
i-C_4H_{10}—MCH($10^{a)}$)	3.94	0.87	—
	3.94	0.94	—
i-C_4H_{10}—MCH($10^{a)}$)—SF_6($3^{a)}$)	4.11	0.81	—
	4.06	0.74	—
i-C_4H_{10}—MCH($10^{a)}$)—N_2O($3^{a)}$)	4.00	$0.78^{b)}$	$1.62^{b)}$
	4.20	$0.78^{b)}$	$1.43^{b)}$

a) Unit, mol/100 mol of i-C_4H_{10}

b) It is assumed that the efficiency of N_2O(3 mol/100 mol of i-C_4H_{10}) is approximately the same as that of SF_6 (3 mol/100 mol of i-C_4H_{10}).
$G(CH_4)$ from non-ionic process in the radiolysis of i-C_4H_{10}—MCH($10^{a)}$)—N_2O($3^{a)}$) system, therefore, is assumed to be the same as that in the radiolysis of i-C_4H_{10}—MCH($10^{a)}$)—SF_6($3^{a)}$) system.
$G(N_2)$ is obtained by the relation:
$G(N_2)=G(N_2+CH_4)_{i\text{-}C_4H_{10}\text{—MCH}(10^{a)})\text{—}N_2O(3^{a)})\text{ system}} - G(CH_4)_{i\text{-}C_4H_{10}\text{—MCH}(10^{a)})\text{—}SF_6(3^{a)})\text{ system}}$

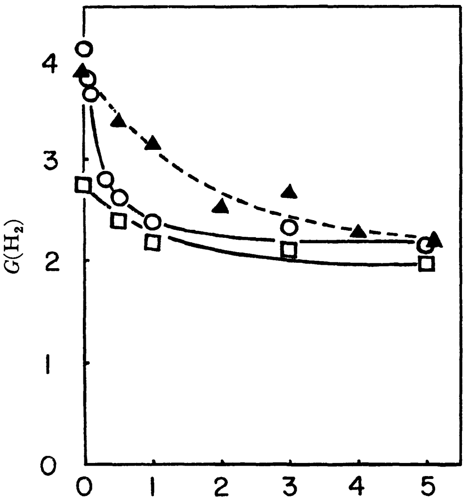
---

[1] a) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **42**, 1164 (1969). b) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, *ibid.*, **43**, 1017 (1970).

[2] a) T. Miyazaki, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.*, **42**, 2086 (1969). b) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **74**, 3584 (1970). c) Y. Saitake, T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **44**, 301 (1971).

in the radiolysis of liquid cyclohexane.[3] Therefore, it can be concluded that hydrogen is not formed by the neutralization reaction in the radiolysis of isobutane in the glassy state as it is in the crystalline state.[1]

The effect of CCl_4 on the yield of hydrogen in the radiolysis of isobutane in the liquid, glass, and polycrystal are shown in Fig. 1. Since a part of the hydrogen formation in the radiolysis of liquid isobutane[4] is due to the neutralization reaction of cation and an electron, SF_6 was added in order to suppress the formation of hydrogen by the ionic process. Since the hydrogen is not formed in the radiolysis of the glassy and polycrystalline states by the neutralization reaction, the effect of CCl_4 is not influenced by the presence of an electron scavenger such as N_2O.



Concn. of CCl_4, mol/100 mol of i-C_4H_{10}

Fig. 1. Effect of CCl_4 on the hydrogen formation in the radiolysis of isobutane. Total dose: 4.3×10^6 rad.

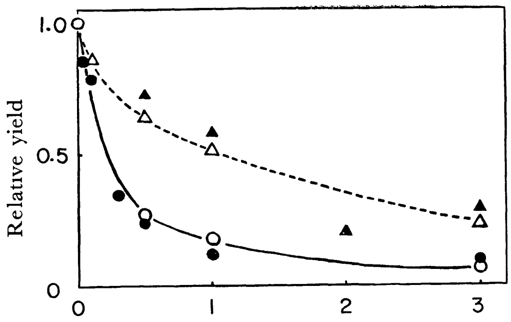
○—○: i-C_4H_{10}—MCH($10^{a)}$)—N_2O($3^{a)}$) system in the glass at 77°K

□—□: i-C_4H_{10}—SF_6($3^{a)}$) system in the liquid at 195°K

▲—▲: i-C_4H_{10} in the polycrystal at 77°K[1]

a) Unit, mol/100 mol of i-C_4H_{10}

Formation of C_4H_9 Radical. The effects of CCl_4 on the yields of t-C_4H_9 radicals in the radiolysis of the i-C_4H_{10}-MCH (4 mol/100 mol of i-C_4H_{10}) system in the glass are shown in Fig. 2. The correlation between the yields of H_2 and those of the C_4H_9 radicals, as plotted against the concentration of CCl_4, is also shown in Fig. 2. Since the effect of CCl_4 on the yields of H_2 is completed at 5 mol of CCl_4/100 mol of i-C_4H_{10}, the yield of hydrogen $G'(H_2)$, which is affected by the addition of CCl_4, can be estimated by the following equation: $G'(H_2)=G(H_2)-G(H_2)_c$. $G(H_2)_c$ is $G(H_2)$ at 5 mol of CCl_4/100 mol of i-C_4H_{10}, and $G'(H_2)$ and $G(C_4H_9)$ are, in the absence of CCl_4, both normalized to unity. The fact that the yields of the C_4H_9 radicals coincide fairly well with $G'(H_2)$ indicates that the formation of the C_4H_9 radical is closely related to the formation of H_2.



Concn. of CCl_4, mol/100 mol of i-C_4H_{10}

Fig. 2. Effect of CCl_4 on the C_4H_9 radical formation in the radiolysis of solid isobutane at 77°K. $G'(H_2)$ is plotted for comparison. Total dose: 1.7×10^5 rad.

○—○: Yields of C_4H_9 radicals in the γ-irradiated i-C_4H_{10}—MCH($4^{a)}$) glass

● : $G'(H_2)$ in the γ-irradiated i-C_4H_{10}—MCH($10^{a)}$)—N_2O($3^{a)}$) glass

△—△: Yields of C_4H_9 radicals in the γ-irradiated i-C_4H_{10} polycrystal[1]

▲ : $G'(H_2)$ in the γ-irradiated i-C_4H_{10} polycrystal[1]

a) Unit, mol/100 mol of i-C_4H_{10}

Discussion

Excitation Transfer. It can be considered that the C_4H_9 radical and H_2 are formed mainly by the decomposition of excited molecules produced directly by the γ-irradiation of solid isobutane. This conclusion is based on the following observations, made both here and in a previous study:[1]

1) The yields of the C_4H_9 radical in the radiolysis of polycrystalline isobutane are not changed by the presence of conventional electron scavengers, such as phenyl iodide, ethyl iodide, nitrous oxide, and sulfur hexafluoride.[1]

2) The yields of the C_4H_9 radical do not increase upon the photobleaching of toluene anions in the γ-irradiated isobutane-toluene(5 mol/100 mol of i-C_4H_{10}) system in the polycrystalline state.[1]

3) The yields of the C_4H_9 radical do not increase upon the photobleaching of electrons trapped in the γ-irradiated isobutane-MCH(4 mol/100 mol of i-C_4H_{10}) system in the glassy state or the photobleaching of benzene anions in the γ-irradiated isobutane-MCH (4 mol/100 mol of i-C_4H_{10})-benzene(5 mol/100 mol of i-C_4H_{10}) system in the glassy state.

4) The yields of H_2 in the radiolysis of glassy isobutane are not changed at all by the presence of conventional electron scavengers, such as nitrous oxide and sulfur hexafluoride.

The yields of the C_4H_9 radical and H_2 decrease sharply, however, upon the addition of CCl_4 in the radiolysis of solid isobutane (Figs. 1 and 2). Let us ascribe this effect to excitation transfer from the excited isobutane molecule to CCl_4 and the suppression of the decomposition of the excited isobutane:

$$C_4H_{10} \overset{I}{\rightsquigarrow} C_4H_{10}^* \tag{3}$$

$$C_4H_{10}^* \xrightarrow{k_d} C_4H_9 + H \tag{4}$$

$$H + H \longrightarrow H_2 \tag{5}$$

$$H + C_4H_{10} \longrightarrow C_4H_9 + H_2 \tag{6}$$

---

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

[4] K. Tanno, S. Shida, and T. Miyazaki, *J. Phys. Chem.*, **72**, 3496 (1968).

$$C_4H_{10}^* + CCl_4 \xrightarrow{k_q} C_4H_{10} + CCl_4^* \tag{7}$$

where I is the rate of reaction (3) and where k is the rate constant. The yield of the thermal hydrogen atom captured by ethylene is measured by ESR and found to be rather small in the radiolysis of i-C_4H_{10} containing C_2H_4.[1] Therefore, it is likely that some of the H atoms in reaction (4) are hot atoms.

As is shown in Fig. 1, the efficiency of excitation transfer depends upon the phases; its order in this system is as follows:

glass > crystal > liquid

The reason why the excitation transfer is more efficient in the glass than in the crystal is not clear at present. It is noted that the yields of hydrogen do not decrease upon the addition of CCl_4 in the liquid phase (Fig. 1).

The C–H bond rupture of the excited butane molecule in reaction (4) may occur in the period of one vibration ($\sim 10^{-13}$ sec). Since the excitation transfer in reaction (7) competes with reaction (4), the rate of excitation transfer is probably extremely high. Therefore, the mechanism of the excitation transfer may be exciton transfer.

Now let us consider the excitation transfer in the glass by the kinetic treatment on hydrogen formation. The formation of hydrogen may be expressed as in reactions (3)—(7). The rate of excitation transfer (reaction (7)) cannot be expressed a priori, as that of the bimolecular reaction. Therefore, the following expression is adopted:[5]

$$R_q = k_q[C_4H_{10}^*][CCl_4]^{n/3} \tag{I}$$

where R_q is the rate of reaction (7). Since the rate of excitation transfer is usually expressed as some integral power function of the distance between two interacting molecules, it is assumed here that $R_q \propto [CCl_4]^{n/3}$, where n is an integer. $[CCl_4]^{1/3}$ is proportional to the reciprocal of the average distance between the molecules of carbon tetrachloride and excited butane. The rate of excitation transfer for various theoretical models is expressed as follows:[6]

a) Exciton transfer:

$$R_q \propto \frac{1}{r^3}$$

b) Vibrational-relaxation resonance transfer:

$$R_q \propto \frac{1}{r^6}$$

where r is the distance between interacting molecules. The steady-state treatment leads to:

$$\frac{1}{G'(H_2)} = \frac{1}{I} + \frac{k_q}{Ik_d}[CCl_4]^{n/3} \tag{II}$$

where n is taken to be 3 or 6, depending upon the models. Kinetic plots of our data for (a) and (b) are shown in Fig. 3. The experimental points fall reasonably well on a straight line for $n=3$; thus,

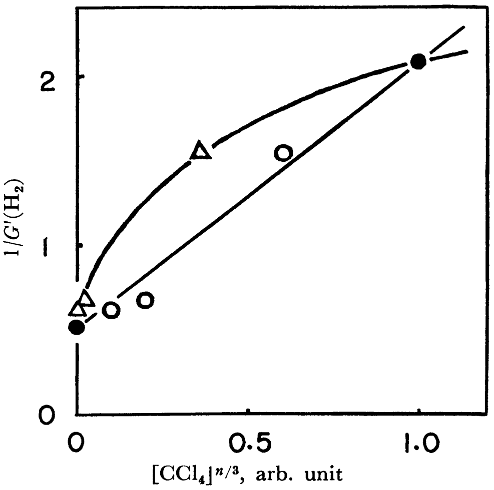


Fig. 3. Relations between $1/G'(H_2)$ and $[CCl_4]^{n/3}$ in the radiolysis of i-C_4H_{10}—MCH(10$^{a)}$)—N_2O(3$^{a)}$) system at 77°K. When $[CCl_4]=0.5^{a)}$, $[CCl_4]^{n/3}$ is nomalized to be 1.

○—○: $n=3$

△—△: $n=6$

a) Unit, mol/100 mol of i-C_4H_{10}

$$R_q \propto [CCl_4] \propto \frac{1}{r^3}$$

The kinetic treatment suggests that the mechanism of excitation transfer in the glass is exciton transfer. The same conclusion was previously obtained for the butyl-radical formation in the crystalline state.[1]

Primary Process of Ionization in the Radiolysis of Solid Hydrocarbons. There are some peculiar phenomena in the solid-state radiolysis, as compared with the radiolysis in the liquid phase.

First, the fragmentation of an excited isobutane ion is negligible in the radiolysis of isobutane in the polycrystal and glass,[1,2b] while it plays an important role in the radiolysis of liquid isobutane.[4] The excited isobutane ion has an electronic excitation energy of more than 1.8 eV and decomposes instantaneously in one vibration to form the $C_3H_7^+$ ion and the CH_3 radical.[7] When the excited isobutane ion is produced by the charge-transfer reaction from Kr^+ in the γ-irradiated Kr-i-C_4H_{10} system at 77°K, it has an excitation energy of more than 1.8 eV and decomposes even in the solid matrix of Kr.[8] Since it seems that the matrix of the i-C_4H_{19}-MCH (10 mol/100 mol of i-C_4H_{10}) system is softer than that of solid Kr at 77°K, we cannot ascribe the depression of the fragmentation of excited ion in the γ-irradiated glassy isobutane to the cage effect by the matrix. Therefore, it is conceivable that the yields of the excited ion are lower in the solid state than in the liquid state.

Second, the yields of hydrogen, which are not affected by the addition of N_2O and which correspond to those from nonionic processes, are much higher in the γ-irradiated glassy isobutane than in the liquid state. Therefore, it is conceivable that the yields of

---

[5] U. A. Kolanovsky and L. S. Polak, *Dokl. Akad. Nauk SSSR*, **135**, 361 (1960).

[6] a) M. Kasha, *Radiat. Res.*, **20**, 55 (1963). b) Th. Förster, "Comparative Effects of Radiation" (M. Burton, J. S. Kirby-Smith, and J. L. Magee, Eds.), John Wiley & Sons, New York, (1960), p. 300.

[7] a) T. Miyazaki, K. Tanno, and S. Shida, This Bulletin, **42**, 362 (1969). b) T. Miyazaki, T. Kohama, K. Fueki, and Z. Kuri, *ibid.*, **42**, 894 (1969).

[8] T. Wakayama, A. Miwa, T. Miyazaki, K. Fueki, and Z. Kuri, unpublished results.

the nonionic species are higher in the solid state than in the liquid state.

Third, it has been reported by several investigators that the yields of the electrons which can be captured by electron scavengers are 1.5—2.0 G-units in the radiolysis of hydrocarbon glasses at 77°K. They used biphenyl,[9] alkyl disulfide,[10] benzene,[11] iodobenzene,[12] and nitrous oxide[12] as electron scavengers. The yields of the electrons captured by these scavengers were determined by measurements of the optical[9,10] or ESR absorption[11] of the anions, or by product analysis.[12] It is very interesting that G(e) values obtained by different scavengers and measurements are 1.5—2.0 in the γ-irradiated hydrocarbon glasses, while the G(e) values amount to 3—4 in γ-irradiated liquid hydrocarbon. Therefore, it is conceivable that the yields of ionization may be smaller in the solid state than in the liquid state.

One possible explanation of these characteristic phenomena of solid radiolysis will be given here from the viewpoint of the formation of the exciton. It may be said, from the above considerations, that the exciton plays an important role in the γ-irradiated solid, though it plays only a minor role in the liquid phase. When the exciton is formed by γ-irradiation in the solid hydrocarbon, the electronic absorption spectrum of the solid can be expected to differ from that of the liquid; that is to say, Davydov splitting can be expected to occur.[13] If a fraction of the ionization occurs from superexcited states, as proposed by Platzman,[14] and if the state of the exciton corresponds to the superexcited state, the following schemes may represent the ionization of i-C_4H_{10}: In the liquid state:[4]

$$i\text{-}C_4H_{10} \rightsquigarrow C_4H_{10}^{**} \tag{8}$$

$$C_4H_{10}^{**} \longrightarrow C_4H_{10}^{+*} + e^- \tag{9}$$

$$\longrightarrow C_4H_{10}^{+} + e^- \tag{10}$$

$$C_4H_{10}^{+*} \longrightarrow C_3H_7^{+} + CH_3 \tag{11}$$

where $C_4H_{10}^{**}$ represents isobutane in the superexcited states and where $C_4H_{10}^{+*}$ represents the excited isobutane ion. In the solid state:

$$i\text{-}C_4H_{10} \rightsquigarrow C_4H_{10}^{*} \tag{3}$$

$$C_4H_{10}^{*} \longrightarrow C_4H_9 + H \tag{4}$$

$$\longrightarrow C_4H_{10}^{+} + e^- \tag{12}$$

where $C_4H_{10}^{*}$ represents the exciton which produces mainly a butyl radical, a hydrogen atom, a butane ion, and an electron. A mechanism by which the exciton may be related to the ionization was also suggested in the solid radiolyses of polyethylene[15] and succinic acid.[16]

It can be understood from the above reaction scheme that the fragmentation of the excited ion occurs only in the radiolysis of liquid isobutane. The yields of hydrogen from nonionic processes may be larger in the radiolysis of solid isobutane than in that of the liquid phase, because reaction (4) is involved. Since the exciton produces mainly neutral fragments in the radiolysis of glass (reaction (4)), the yields of electrons may be rather low in γ-irradiated glass as compared with those in the liquid phase.

The authors wish to thank Dr. Kanji Katsuura of the Kurashiki Rayon Company for his helpful discussions.

---

[9] J. P. Guarino and W. H. Hamill, *J. Amer. Chem. Soc.*, **86**, 777 (1964).

[10] T. Shida, *J. Phys. Chem.*, **74**, 3055 (1970).

[11] T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, This Bulletin, **43**, 3761 (1970).

[12] T. Kimura, T. Miyazaki, K. Fueki, and Z. Kuri, *ibid.*, **41**, 2861 (1968).

[13] A. S. Davydov, "Theory of Molecular Excitons," (translated by M. Kasha and M. Oppenheiner, Jr.) McGraw-Hill Book Company, New York, 1962.

[14] R. Platzman, *Radiat. Res.*, **17**, 419 (1962).

[15] a) R. H. Partridge, *J. Chem. Phys.*, **52**, 2485 (1970). b) R. H. Partridge, *ibid.*, **52**, 2491 (1970).

[16] a) T. Miyazaki, S. Okada, T. Wakayama, K. Fueki, and Z. Kuri, This Bulletin, **43**, 1907 (1970). b) T. Miyazaki, Y. Fujitani, T. Wakayama, K. Fueki, and Z. Kuri, *ibid.*, **43**, 984 (1971).