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Excitation Transfer in the Radiolysis of Solid Hydrocarbons as Studied by ESR Spectroscopy and Product Analysis

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The effect of carbon tetrachloride on the radiolysis of isobutane and methylcyclohexane at 77°K is studied by ESR spectroscopy and by product analysis. The yields of solvent radicals from the γ-irradiation of isobutane and methylcyclohexane are not changed by the presence of conventional electron scavengers. This indicates that solvent radicals are not formed by the neutralization of solvent cations with electrons. On the contrary, the yields of solvent radicals decrease remarkably upon the addition of CCl_4. Though the yield of propylene from the γ-irradiation of isobutane is not affected by the addition of electron scavengers, it decreases significantly upon the addition of CCl_4. Though the decrease in the hydrogen yield in the radiolysis of methylcyclohexane at 77°K upon the addition of electron scavengers is only about 1G-unit, it amounts to more than 3.5G-units upon the addition of CCl_4. These characteristic effects of CCl_4 can possibly be explained in terms of excitation transfer from the excited solvent molecule to CCl_4. A kinetic treatment suggests that its mechanism may be an exciton transfer.

Product analysis and the observation of reaction intermediates have been two major methods for the study of the reaction mechanism of radiolysis. Since these two methods reveal different aspects of mechanisms, however, it is desirable to make a study of the radiolysis mechanism using both methods. Along this line we have previously studied the reaction of nitrous oxide with electrons in organic glass[1] and the radiolysis of phenylacetate in the solid states[2] at −196°C.

We reported in a previous communication[3] that the yield of the isobutyl radical produced in γ-irradiated isobutane at −196°C decreases upon the addition of carbon tetrachloride, while it is not affected by the addition of other electron scavengers, such as nitrous oxide, sulfur hexafluoride, and ethyl iodide. Here we will study in more detail, by ESR spectroscopy and by product analysis, the characteristic effect of carbon tetrachloride in the radiolysis of isobutane and methylcyclohexane at −196°C.

Experimental

The isobutane and the methylcyclohexane were more than 99.9% pure. The gas-chromatographic analysis did not show any detectable impurity. They were used after degassing and distillation on a vacuum line. The carbon tetrachloride (99.9%) was used after vacuum distillation. The additives, such as phenyl iodide, ethyl iodide, nitrous oxide, sulfur hexafluoride, *n*-butyl chloride, carbon dioxide, and ethylene, were all of a high purity and were used after vacuum distillation.

The samples were irradiated with γ-rays from Co-60 at a dose rate of 4.2×10^5 rad/hr. The photobleaching of the γ-irradiated samples was carried out at 77°K with the light from a tungsten lamp.

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 cupric oxide furnace kept at 240°C. The hydrocarbon products were analyzed by a Hitachi K53 gas chromatograph equipped with a flame-ionization detector (activated alumina column, 2 m, 100°C).

The *G*-value is expressed here by the number of product molecules per 100 eV absorbed in isobutane or methylcyclohexane. The *G*-values of the radicals were determined by ESR measurements by assuming $G(\text{radical})=1.6$ for the radicals produced in the γ-irradiated 3-methylpentane at −196°C.[4]

Results and Discussion

Radiolysis of Isobutane. *A) The Effect of Carbon Tetrachloride on Solvent Radical Formation.* Isobutane forms a polycrystal at −196°C, and when irradiated with γ-rays it produces the isobutyl

1) T. Wakayama, T. Kimura, T. Miyazaki, K. Fueki and Z. Kuri, This Bulletin, **42**, 266 (1969).

2) Y. Noro, M. Ochiai, T. Miyazaki, A. Torikai, K. Fueki and Z. Kuri, *J. Phys. Chem.*, **74**, 63 (1970).

3) T. Wakayama, T. Miyazaki, K. Fueki and Z. Kuri, This Bulletin, **42**, 1164 (1969).

4) M. Shirom and J. E. Willard, *J. Phys. Chem.*, **72**, 1702 (1968).

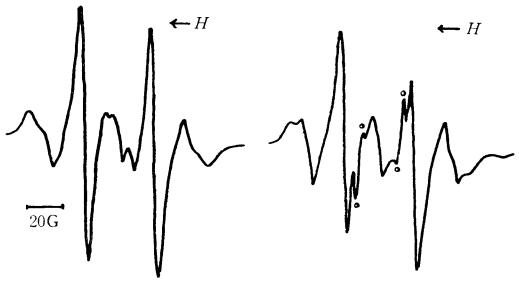

Fig. 1. (A) Fig. 1. (B)

Fig. 1. A) ESR spectrum of isobutyl radical in the radiolysis of isobutane at 77°K.
B) ESR spectrum of γ-irradiated isobutane containing 4.8 mol% ethylene at 77°K. ○-represents main signals of ethyl radical.
Dose: 1.7×10^5 rad.

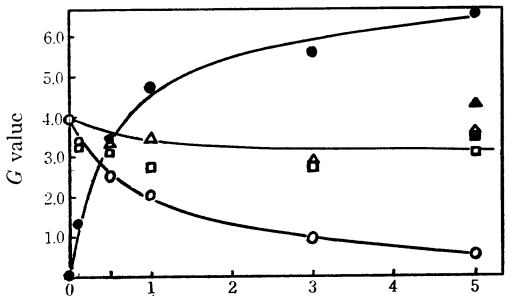

Fig. 2. Effect of additives on the formation of radical in the radiolysis of isobutane at 77°K studied by ESR.
Dose: 1.7×10^5 rad.
Yields of isobutyl radical are shown by the following plots:
○ CCl_4
△ C_6H_5I
□ C_2H_5I
▲ N_2O
■ SF_6
} Additives
Yields of CCl_3 radical in the radiolysis of i-C_4H_{10}-CCl_4 system are also shown by plots (●).

radical whose ESR spectrum is shown in Fig. 1(A). The yield of the isobutyl radical is not affected by the addition of electron scavengers, such as phenyl iodide, C_2H_5I, N_2O, and SF_6 (Fig. 2). When isobutane containing ethyl iodide was γ-irradiated at −196°C, an ethyl radical was observed by ESR measurement. The ethyl radical is produced by dissociative electron attachment to ethyl iodide (reactions (1) and (2)).

$$C_4H_{10} \rightsquigarrow C_4H_{10}^+ + e^- \quad (1)$$

$$e^- + C_2H_5I \longrightarrow C_2H_5 + I^- \quad (2)$$

Nitrous oxide suppresses the formation of the toluene anion in the γ-irradiated isobutane-toluene system, as will be described in the next section, and it also acts as an effective electron scavenger.

Therefore, it can be said that the isobutyl radical is not produced by the neutralization reaction in the radiolysis of solid isobutane. The effect of CCl_4 on the formation of isobutyl radical is shown in Fig. 2. Here the remarkable points are the rapid decrease in the yield of the solvent radical and the increase in the yield of the CCl_3 radical with the increase in the concentration of CCl_4. The yield of the CCl_3 radical amounts to 6.5G-units at $[CCl_4]=5$ mol/100 mol of i-C_4H_{10}. The large yield of the CCl_3 radical cannot be explained only by the dissociative electron attachment:

$$e^- + CCl_4 \rightarrow CCl_3 + Cl^- \quad (3)$$

but suggests the participation of some other reactions. Since the ionization potential of isobutane (10.8 eV) is lower than that of carbon tetrachloride (11.5 eV), isobutane ion in the ground state cannot transfer its charge to CCl_4. The quantity of mobile excited butane ions is considered to be rather small because of the fact that the toluene cation was not formed in the γ-irradiated isobutane matrix containing toluene (*cf.* next section). Therefore, the effect of CCl_4 on the formation of the isobutyl radical may not be due to charge transfer from the excited isobutane ion to carbon tetrachloride.

Let us tentatively ascribe this effect to excitation transfer from the excited isobutane molecule to carbon tetrachloride and the suppression of the decomposition of the excited isobutane (reactions (4)—(6)):

$$C_4H_{10} \rightsquigarrow C_4H_{10}^* \quad (4)$$

$$C_4H_{10}^* \longrightarrow C_4H_9 + H \quad (5)$$

$$C_4H_{10}^* + CCl_4 \longrightarrow C_4H_{10} + CCl_4^* \quad (6)$$

A portion of CCl_4^* may decompose further to produce CCl_3 and Cl radicals:

$$CCl_4^* \rightarrow CCl_3 + Cl \quad (7)$$

The presence of H atoms produced in reaction (5) is demonstrated by the fact that the ethyl radical is observed by ESR measurements in the γ-irradiated isobutane-ethylene system (Fig. 1(B)):

$$H + C_2H_4 \rightarrow C_2H_5 \quad (8)$$

B) The Effect of Toluene on Solvent Radical Formation. The effect of toluene on the formation of the isobutyl radical is shown in Figs. 3 and 4. Here the remarkable points are the rapid decrease in the yield of the solvent radical and the appearance of a new ESR spectrum with the increase in the concentration of toluene. The new spectrum disappears easily upon illumination with light from a tungsten lamp, and it decreases upon the addition of nitrous oxide to the i-C_4H_{10}-$C_6H_5CH_3$ system (Fig. 4a, b and c). These results suggest that the species responsible for this spectrum may be assigned to the toluene anion. The spectrum consists of five lines with a splitting constant of 4.2 G.

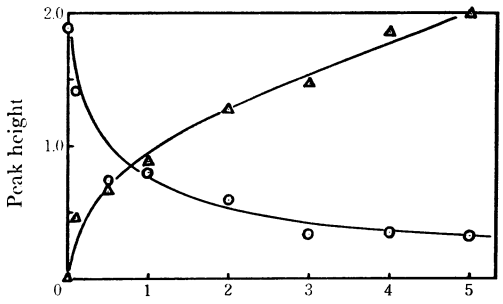

Fig. 3. Effect of toluene on the formation of radical in the radiolysis of isobutane at 77°K studied by ESR.
Dose: 1.7×10^5 rad.
○, isobutyl radical; △, toluene anion

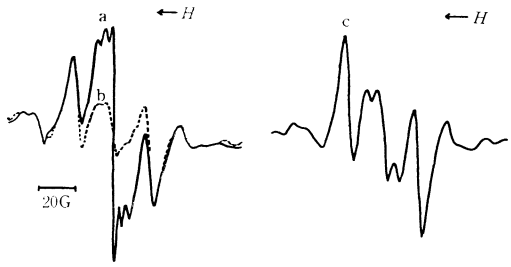

Fig. 4. a) ESR spectrum of γ-irradiated isobutane containing 4.8 mol% toulene at 77°K.
b) The same sample as (a) after 5 min illumination with visible light.
c) ESR spectrum of γ-irradiated isobutane - toluene (4.8 mol%) - nitrous oxide (0.9 mol%) system at 77°K.
Dose: 1.7×10^5 rad.

The ESR spectrum of the toluene anion produced chemically consists mainly of five lines with a splitting constant of 4.0 G,[5] these lines arising from hyperfine interactions with ortho- and meta-protons. The formation of the toluene anion and the related reactions may be written as follows:

$$i\text{-}C_4H_{10} \rightsquigarrow C_4H_{10}^+ + e^- \quad (9)$$

$$e^- + C_6H_5CH_3 \rightarrow C_6H_5CH_3^- \quad (10)$$

$$C_6H_5CH_3^- \xrightarrow[\text{(visible light)}]{h\nu} C_6H_5CH_3 + e^- \quad (11)$$

$$e^- + N_2O \rightarrow N_2 + O^- \quad (12)$$

The absence of the toluene cation suggests that the amount of the mobile excited ion may be negligibly small in the γ-irradiated solid isobutane. Since the yield of isobutyl radical is not altered by the photodetachment of an electron from a toluene anion (reaction (11)), the isobutyl radical is not formed by the neutralization of an electron with an isobutane cation.

5) S. P. Solodovnikov, *Zh. Strukt. Khim.*, **2**, 282 (1961).

Since the addition of toluene suppresses the formation of the isobutyl radical, as does carbon tetrachloride, toluene may also act as an acceptor of excitation energy:

$$C_4H_{10}^* + C_6H_5CH_3 \rightarrow C_4H_{10} + C_6H_5CH_3^* \quad (13)$$

C) The Effect of Carbon Tetrachloride on the Final Products. The fragment products in the radiolysis of isobutane at −196°C are mainly hydrogen, methane, propane, propylene, and isobutene. The hydrogen and propylene decrease in amount upon the addition of CCl_4 (Figs. 5 and 6). The

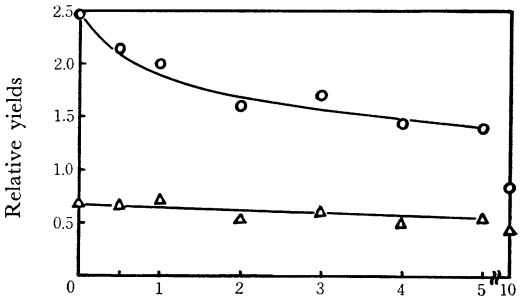

Fig. 5. Effect of CCl_4 on the formation of hydrogen and methane in the radiolysis of isobutane at 77°K.
Dose: 3.4×10^6 rad.
○, H_2; △, CH_4

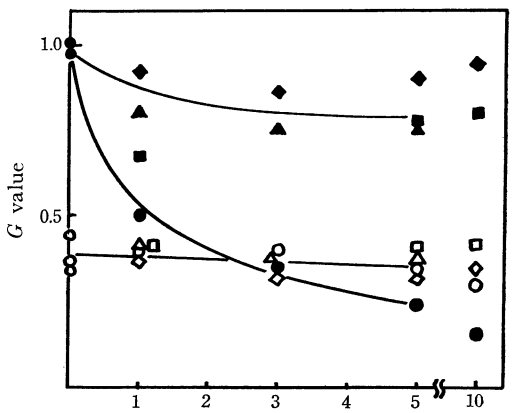

Fig. 6. Effect of additives on the formation of propylene and propane in the radiolysis of isobutane at 77°K.
Dose: 3.4×10^6 rad.

Yields of C_3H_6	Yields of C_3H_8
● CCl_4	○ CCl_4
▲ C_2H_5I	△ C_2H_5I
■ SF_6	□ SF_6
◆ N_2O	◇ N_2O

fact that the yield of propylene is not affected by the addition of electron scavengers, such as N_2O, SF_6, and C_2H_5I, indicates the absence of the follow-

ing neutralization reactions:

$$C_4H_{10}^+ + e^- \rightarrow C_3H_6 + CH_4 \quad (14)$$

$$C_3H_7^+ + e^- \rightarrow C_3H_6 + H \quad (15)$$

The yield of propane in the radiolysis of isobutane at −196°C are 0.3—0.4 G-unit in the presence of SF_6, while the yields amount to 1.4 in the radiolysis in the liquid phase.[6] This is because the fragmentation of the electronically-excited isobutane ion (reaction (16)) may be suppressed in the solid state by the dissipation of the electronic excitation energy to the solvent matrix; thus, the reaction of the $C_3H_7^+$ ion, reaction (15), for example, may play a minor role in the radiolysis of solid isobutane:

$$C_4H_{10}^{+*} \rightarrow C_3H_7^+ + CH_3 \quad (16)$$

The possibility that propylene may be produced directly from the fragmentation of the excited isobutane ion may be unimportant for two reasons. (i) The amounts of the CH_4^+ and $C_3H_5^+$ ions are rather small in the mass spectrum of isobutane, which may be correlated to C_3H_6 (reactions (17)—(20)):

$$C_4H_{10} \rightsquigarrow C_4H_{10}^{+*} + e^- \quad (17)$$

$$C_4H_{10}^{+*} \longrightarrow C_3H_6 + CH_4^+ \quad (18)$$

$$\searrow\ C_3H_5^+ + CH_3 + H_2 \quad (19)$$

$$C_3H_5^+ + C_4H_{10} \longrightarrow C_3H_6 + C_4H_9^+ \quad (20)$$

(ii) Even if $C_4H_{10}^{+*}$ is formed, its fragmentation may be suppressed in the condensed phase by collisional deactivation (reaction (21)).[7]

$$C_4H_{10}^{+*} + C_4H_{10} \rightarrow C_4H_{10}^+ + C_4H_{10} \quad (21)$$

It is suggested, therefore, that propylene is formed mainly by the fragmentation of the excited isobutane molecule:

$$C_4H_{10} \rightsquigarrow C_4H_{10}^* \quad (4)$$

$$C_4H_{10}^* \longrightarrow C_3H_6 + CH_4 \quad (22)$$

$$\searrow\ C_3H_6 + CH_3 + H \quad (23)$$

Lias and Ausloos[8] have reported that propylene is one of the main products in the fragmentation of excited or superexcited isobutane molecules in the photolysis of isobutane in the gas phase.

The addition of carbon tetrachloride suppresses the formation of propylene in the radiolysis of solid isobutane. When ethylene (3 mol/100 mol of i-C_4H_{10}) is added to the i-C_4H_{10}-CCl_4 system in order to protect propylene from the occurrence of reaction (24) while the irradiated sample is being warmed to room temperature, CCl_4 suppresses the formation of propylene to the same extent as in the absence of ethylene. This confirms that the effect of CCl_4 is not due to the secondary reaction of propylene with CCl_3 radicals.

$$C_3H_6 + CCl_3 \rightarrow C_3H_6CCl_3 \quad (24)$$

Therefore, the excitation transfer from the excited isobutane molecule to carbon tetrachloride (reaction (6)) may compete with Reactions (22) and/or (23). Since the yield of methane is not affected by the addition of carbon tetrachloride, Reaction (22) may be unimportant in the formation of propylene. The failure to detect the methyl radical, which would be produced by Reaction (23), may be due to its rapid combination with other radicals, for example butyl radicals, in a spur.

Radiolysis of Methylcyclohexane. As is shown in Fig. 7, the yield of solvent radicals decreases

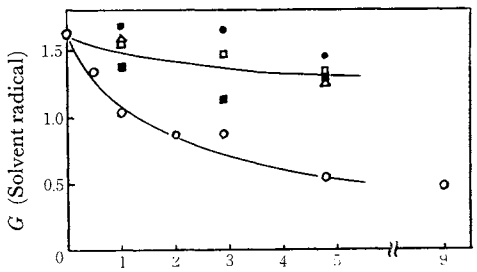

Fig. 7. Effect of additives on the formation of solvent radical in the radiolysis of methylcyclohexane at 77°K studied by ESR.
Dose: 2.1×10^5 rad.
○, CCl_4; □, n-C_4H_9Cl; △, CO_2; ●, N_2O; ■, SF_6

upon the addition of CCl_4. The reaction scheme for the radiolysis of methylcyclohexane may be depicted as follows:

$$C_7H_{14} \rightsquigarrow C_7H_{14}^+, C_7H_{14}^{+*}, C_7H_{14}^*, e^- \quad (25)$$

$$\left.\begin{matrix} C_7H_{14}^+ \\ C_7H_{14}^{+*} \end{matrix}\right\} + e^- \longrightarrow C_7H_{14}^* \quad (26)$$

$$C_7H_{14}^* \longrightarrow C_7H_{13} + H \quad (27)$$

$$\searrow\ C_7H_{12} + H_2 \quad (28)$$

$$2H \longrightarrow H_2 \quad (29)$$

The electron scavengers, such as CO_2, N_2O, SF_6, and n-C_4H_9Cl, but not CCl_4, do not suppress the yield of the solvent radical (Fig. 7). In these cases it was found, by ESR or product analysis, that CO_2^-, N_2,[9] and n-C_4H_9 radicals are formed by electron attachement to CO_2, N_2O, and n-C_4H_9Cl respectively. Moreover, when the trapped electron is bleached by infrared light, the solvent radical does not increase. Therefore, it can be said that the solvent radical is not produced by the neutralization reaction, (26).

6) a) K. Tanno, S. Shida and T. Miyazaki, *J. Phys. Chem.*, **72**, 3496 (1968). b) T. Miyazaki, K. Tanno and S. Shida, This Bulletin, **42**, 362 (1969).

7) T. Miyazaki, *J. Phys. Chem.*, **71**, 4283 (1967).

8) S. G. Lias and P. Ausloos, *J. Chem. Phys.*, **48**, 392 (1968).

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

The characteristic effects of CCl_4 in the radiolysis of methylcyclohexane at 77°K were also observed on the production of hydrogen (Fig. 8). The

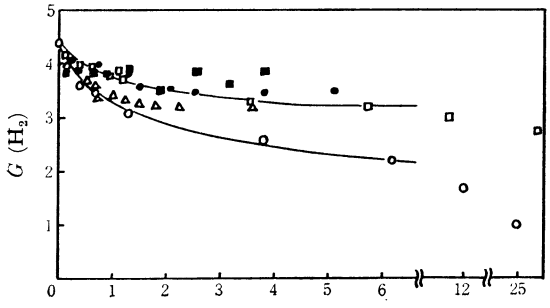

Fig. 8. Effect of additives on the formation of hydrogen in the radiolysis of methylcyclohexane at 77°K.
Dose: 3.6×10^5 rad.
○, CCl_4; □, n-C_4H_9Cl; △, C_6H_5I; ■, SF_6; ●, N_2O

decrease in the amount of hydrogen upon the addition of CCl_4 exceeds 3.5 G-units at the highest concentration, while the decreases upon the addition of n-C_4H_9Cl, SF_6, N_2O,[9] and C_6H_5I[9] are 1.3, 0.7, 0.8, and 1.3 G-units respectively.

Since the ionization potential of methylcyclohexane (9.9 eV) is lower than that of carbon tetrachloride (11.5 eV), the methylcyclohexane ion in the ground state cannot transfer its charge to CCl_4. Though the excited methylcyclohexane ion might transfer its charge to CCl_4, let us tentatively ascribe the effect of CCl_4 to the excitation transfer (reaction (30)):

$$C_7H_{14}^* + CCl_4 \longrightarrow C_7H_{14} + CCl_4^* \qquad (30)$$

Mechanism of Excitation Transfer. From the above results it can be assumed that the isobutyl radical is formed mainly by the decomposition of excited molecules in the radiolysis of solid isobutane and that CCl_4 acts as an acceptor of the excitation energy. Recently it was found, in a study of ultraviolet-induced luminescence of benzene, that CCl_4 is an efficient excitation quencher.[10] The mechanism of excitation transfer will now be discussed on the basis of the effect of CCl_4 on the formation of the isobutyl radical. A possible kinetic scheme is the following:

$$C_4H_{10} \xrightarrow{I} C_4H_{10}^* \qquad (4)$$

$$C_4H_{10}^* \xrightarrow{k_d} C_4H_9 + H \qquad (5)$$

$$C_4H_{10}^* + CCl_4 \xrightarrow{k_q} C_4H_{10} + CCl_4^* \qquad (6)$$

where I is the rate of reaction (4) and where k is the rate constant. The rate of excitation transfer (reaction (6)) cannot be expressed *a priori* as that of the bimolecular reaction. Therefore, the following expression may be adopted:[11]

$$R_q = k_q\,[C_4H_{10}^*][CCl_4]^{n/3} \qquad (I)$$

where R_q is the rate of reaction (6). Since the rate of excitation transfer is usually some integral power function of the distance between two interacting molecules, it is natural to assume $R_q \propto [CCl_4]^{n/3}$, 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 may be expressed as follows:[12]

a) Exciton transfer:

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

b) Vibrational-relaxation resonance transfer:

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

c) Polak's treatment:[11]

$$R_q \propto \frac{1}{r^2}$$

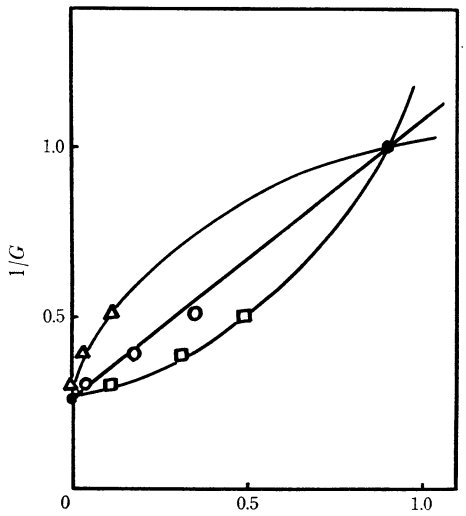

Fig. 9. Relations between $1/G(C_4H_9)$ and $[CCl_4]$. When $[CCl_4]=0.45$M, $[CCl_4]^{n/3}$is normalized to be 1.
—△—, $n=6$; —□—, $n=3$; —○—, $n=2$

10) P. K. Ludwig and C. D. Amata, *J. Phys. Chem.*, **72**, 3725 (1968).

11) a) U. A. Kolanovsky and L. S. Polak, *Dokl. Acad. Nauk SSSR*, **135**, 361 (1960). b) "Radiolysis of Hydrocarbons," ed. by A. V. Topchiev, Elsevier Publishing Company, Amsterdam-London-New York (1964), p. 138.

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

where r is the distance between interacting molecules.

The steady-state treatment leads to:

$$\frac{1}{G(C_4H_9)} = \frac{1}{I} + \frac{k_d}{Ik_q}[CCl_4]^{n/3} \qquad (II)$$

where n is taken to be 2, 3, or 6, depending upon the models. Kinetic plots of our data for these cases are shown in Fig. 9. The experimental points fall reasonably well on a straight line for $n=3$; thus,

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

The kinetic treatment suggests that the mechanism of excitation transfer in our system is exciton transfer.

The slope-to-intercept ratio gives $k_q/k_d=7.3\text{M}^{-1}$. The C–H bond rupture of the excited butane molecule may occur in the period of one vibration (10^{-12}—10^{-13} sec). It seems reasonable to assume $k_d=10^{12}$—10^{13} sec^{-1}. Therefore, we obtain:

$$k_q = 7\times10^{12}\text{—}10^{13}\ \text{M}^{-1}\text{sec}^{-1}$$

This suggests that the rate of excitation transfer is extremely high as compared with the rate of diffusion-controlled reactions in the liquid phase ($\sim10^{10}$ M^{-1}sec^{-1}). k_q is of approximately the same order of magnitude as the theoretical value[12] (10^{12}—10^{13}M^{-1} sec^{-1}) of the transfer rate of the localized exciton.