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The Reaction of Recoil ^{35}S Atoms with Organic Compounds. II. The Insertion Reaction of Recoil ^{35}S Atoms into the C–H and C–C Bonds in Ethane in the Gas Phase

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The sulfur atoms produced by the nuclear transformation of ^{35}Cl(n,p)^{35}S were allowed to react with gaseous ethane in the presence or in the absence of radical scavengers. The products were hydrogen sulfide, methanethiol, ethanethiol, dimethyl sulfide, and other sulfur-containing compounds. The yield of the C–H insertion product (ethanethiol) increased upon the addition of a small amount of the scavenger and then decreased with an increase in the amount of the scavenger to give a constant value, but the yield of the C–C insertion product (dimethyl sulfide) did not vary. The increase in the ethanethiol yield at low concentrations of the scavenger may be ascribed to a protective effect by the scavenger. By the addition of ethanethiol before thermal-neutron irradiation, the yield of ethanethiol was increased, but that of dimethyl sulfide was not increased, therefore the primary yield of ethanethiol could be determined. The spin state of the reactive sulfur atoms in the thermal-insertion reaction was also estimated to be the ^{3}P state upon the addition of COS and C_2H_4.

Recently, there have been intensive investigations of the reactivities of the sulfur atoms generated by the photolysis of COS and by nuclear transformations. Kremer and Spicer have studied the reactions of recoil ^{35}S or ^{38}S atoms produced from ^{34}S or ^{40}Ar atoms with several reactants.[1,2]

Church and Rowland have also investigated the reaction of ^{35}S atoms produced from ^{35}Cl atoms with propane; they found that the atoms are predominantly inserted into the secondary C–H bond in the triplet state.[3]

The sulfur atoms generated photolytically from COS can be inserted into the C–H bond of hydrocarbons to produce the corresponding thiols. These insertion reactions have been investigated in detail by Strausz and Gunning;[4] they have established that the atoms can be inserted into the C–H bond in ethane in the singlet state.

In our previous paper,[5] it has been demonstrated that the recoil sulfur atoms produced by the nuclear transformation of ^{35}Cl(n,p)^{35}S in the liquid phase are capable of being inserted into the C–C bond of 2-methylbenzothiazole by the energetic process, and that the insertion into the C–H bond of benzothiazole takes place not only in the energetic process but also in other processes, such as the thermal and the dissociation processes.

In this paper, the primary yield of sulfur compounds in the reaction of the sulfur atoms produced by the nuclear transformation of ^{35}Cl(n,p)^{35}S process with gaseous ethane will be estimated, and the ratio of the insertion rate of the C–H bond to that of the C–C bond will be decided. Also, the spin state of the sulfur atoms in this reaction will be discussed.

Experimental

Materials. Ethane (purchased from the Takachiho Chem. Co.; purity, 99.9%) and dichlorodifluoromethane as a chlorine source (Asahi Glass Co., Ltd.; purity, 99.8%) were purified by trap-to-trap distillation.

Methanethiol, ethanethiol, and dimethyl sulfide were also purified by trap-to-trap distillation before use. Carbonyl sulfide (prepared from KSCN and sulfuric acid) and hydrogen sulfide (prepared from NaSH and hydrochloric acid) were purified by gas-chromatographic separation using a silica-gel column.

Nitrogen monoxide was purified by trap-to-trap distillation, while oxygen from the tank was purified by passing it through a NaOH trap to remove a trace amount of carbon dioxide.

Thermal-neutron Irradiation. Thermal neutron irradiation was carried out by means of a Triga Mark II nuclear reactor (Institute for Atomic Energy, Rikkyo University) at a thermal-neutron flux of about 1.5×10^{12} n cm^{-2} s^{-1} for 1 h.

A mixture of ethane and dichlorodifluoromethane was irradiated in a quartz ampoule (about 5 ml) at a total pressure of about 700 Torr.†

The ratio of the ethane pressure to the dichlorodifluoromethane pressure was 2.05 ± 0.02. Additives were also added to this system. The irradiation was carried out in the gas phase and at a reactor temperature of about 40 °C. The irradiated samples were stored below −78 °C and then at −196 °C until analysis.

The Separation and the Purification of the Reaction Products. Carriers [carbonyl sulfide, hydrogen sulfide, methanethiol, ethanethiol, dimethyl sulfide, carbon disulfide, ethyl methyl sulfide, and diethyl sulfide (about 0.2×10^{-5}—0.5×10^{-5} mol each; Tokyo Kasei Co.; purity, above 98% except for hydrogen sulfide and carbonyl sulfide)] were added to avoid the loss of trace amounts of ^{35}S-labeled compounds during separation and purification. The separation and the purification of the products were performed by means of a gas-chromatograph equipped with a thermal conductivity cell, using hydrogen as the carrier gas. The column contained 15% tritolyl phosphate, 15% *m*-bis(*m*-phenoxy phenoxy) benzene (polyphenyl ether, 5 rings), 15% squalane and 10% α-[4-(1,1,3,3-tetramethyl butyl)phenyl]-ω-hydroxy poly(oxy-1,2-ethanediyl) [Triton-X 305] on Chromosorb-T (40—60 mesh) in stainless steel tubes (3-mm diameter; 7 m, 5 m, 3 m, and 2 m long).

The Reduction of the Reaction Products to $H_2{}^{35}S$.[6] Each eluted sulfur compounds from the gas-chromatograph was passed through quartz tube containing platinized quartz wool as a catalyst and heated above 800 °C to produce hydrogen sulfide-^{35}*S*. The hydrogen sulfide thus produced was trapped at the temperature of liquid nitrogen. The reduction efficiency was about 60—80%.

The Radioassay of the Reaction Products. The amount and the radioactivity of hydrogen sulfide was measured by

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† 1 Torr = 133.3 Pa.

means of a radio-gas-chromatograph equipped with a thermal conductivity cell and with a proportional flow counter. The specific radioactivity of each product was determined by comparing the mass peak area with the radioactivity of the hydrogen sulfide.

The radiochemical yield was determined from the specific radioactivity of each product and the standard hydrogen sulfide obtained by the simultaneous irradiation of ammonium chloride in the following processes:

$$NH_4Cl \xrightarrow{\text{irradiation with thermal neutrons}} {}^{35}S \xrightarrow[\text{oxidation by } HNO_3]{Na_2SO_4\text{(carrier)}}$$

$$^{35}SO_4^{2-} \xrightarrow{BaCl_2 \text{ aq}} Ba^{35}SO_4 \xrightarrow[\text{Pt(catalyst)}]{H_2 \text{ at } 900\,^\circ C} Ba^{35}S^{9)} \xrightarrow[H_3PO_4]{}$$

$$H_2{}^{35}S^{10)}$$

The column for the quantitative determination of the hydrogen sulfide consisted of silica gel (60—80 mesh) in a stainless steel tube (2 m long, 3-mm diameter).

No isotopic exchange was found between the products and the carriers, as confirmed by the following experimental fact. The methanethiol separated gas-chromatographically from a mixture of labeled hydrogen sulfide-^{35}S, ethanethiol-^{35}S and non-radioactive methanethiol did not show any radioactivity under the same experimental conditions as those in the analysis of the reaction product. The standard deviation in the figures represents the experimental error in 2 or more runs.

Results and Discussion

The Effects of the Radical Scavenger. When recoil sulfur atoms react with an organic compound, roughly two processes (thermal and energetic) must be considered. In order to eliminate the thermal process, radical scavengers have been used in a number of recoil and radiation chemical studies. Nitrogen monoxide has been used as a radical scavenger by Hyder and Markowitz in the reactions of recoil sulfur atoms with hydrogen sulfide and other reactants.[11)] Oxygen has been also used by Lee and his coworkers in the reactions of recoil sulfur atoms with CO and CO_2 to produce $CO^{35}S$, especially, it may be said that oxygen reacts fast with the triplet sulfur atoms.[13)]

The effects of the scavenger on the formations of the two insertion products are shown in Fig. 1. The formation of dimethyl sulfide was not affected by the addition of NO, but the yield of ethanethiol was affected by the addition of NO.

The results of the effects of the scavenger show that both the thermal and energetic processes are obviously involved in the formation of ethanethiol, but the thermal process sensitive to NO may not be involved in the formation of dimethyl sulfide. This sulfide formation seems to be inserted directly by means of the recoil sulfur atoms with excess translational energy into the C–C bond.[14)] The insertion of a diradical into the C–C bond in the thermal reaction has not been known. The fact that the C–C insertion takes place only in the energetic process may not conflict with usual chemical reactions. This finding had already been discussed in a previous paper.[5)]

Figure 1 shows that the yield of ethanethiol increases slightly at the low concentration of NO, but as the concentration of NO is increased the yield decreases to about 0.4%. This may be considered to show that the increase is due to a protective effect by the radical scavenger. The main characteristic of the action of NO may be the high reactivity with radicals or fragments, which reduce the thiol yield.

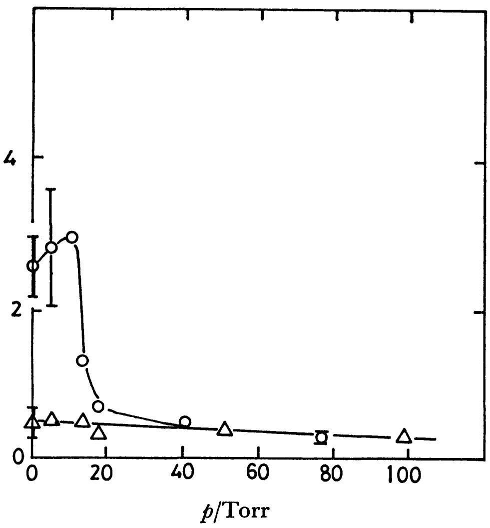

Fig. 1. Plots of the yield of ethanethiol and dimethyl sulfide as a function of NO pressure.
○: Ethanethiol, △: dimethyl sulfide.

Thiols are easily decomposed by radicals and by some other fragments formed in an irradiated system. These types of behavior have also been seen in the reaction of recoil tritium atoms with pure ethane[16)] in the presence of oxygen and in the reactions of recoil carbon atoms with methane[17)] and ammonia,[18)] in which the increases the yields of ethylene-t and methylamine have been ascribed to the protective effect of oxygen.[19)]

The Addition of Thiols and Dimethyl Sulfide. If an additive which is identical with a product is present in the reaction system before the irradiation, the product may be protected from the attack of radicals formed by radiation, and then the primary yield may be estimated, because the number of additive molecules is much greater than that of the product molecules formed in the system. The effects of the additives on the formation of ethanethiol and dimethyl sulfide are shown in Figs. 2—4 in the presence or in the absence of *ca.* 20 Torr oxygen as a radical scavenger. By the addition of ethanethiol the yield of radioactive ethanethiol increased in both the presence and the absence of the radical scavenger.

This increase suggests that the sulfur atoms also react with added thiol by means of the collisional exchange with the sulfur in the added ethanethiol. Then the intercept of the plots of the thiol yield in the scavenged and non-scavenged systems in Fig. 2 may give the primary yield of ethanethiol in the energetic and the sum of the energetic and thermal processes.

The values are 0.4% and 3.7% respectively. The difference in the yield (dotted line) of ethanethiol between that in the presence and that in the absence of the scavenger in Fig. 2 increases slightly. This

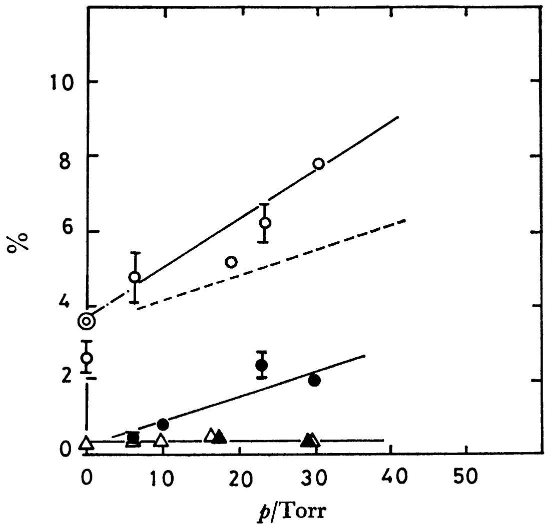

Fig. 2. Plots of the yield of ethanethiol and dimethyl sulfide as a function of the pressure of added ethanethiol or the added dimethyl sulfide in the presence or in the absence of O_2.
○: Ethanethiol in the absence of O_2, ●: ethanethiol in the presence of *ca.* 20 Torr O_2, △: dimethyl sufide in the absence of O_2, ▲: dimethyl sulfide in the presence of *ca.* 20 Torr O_2, ◎: intercept of the plots of ethanethiol yield in the absence of O_2, ……: difference between the yield in the absence of O_2 and in the presence of O_2.

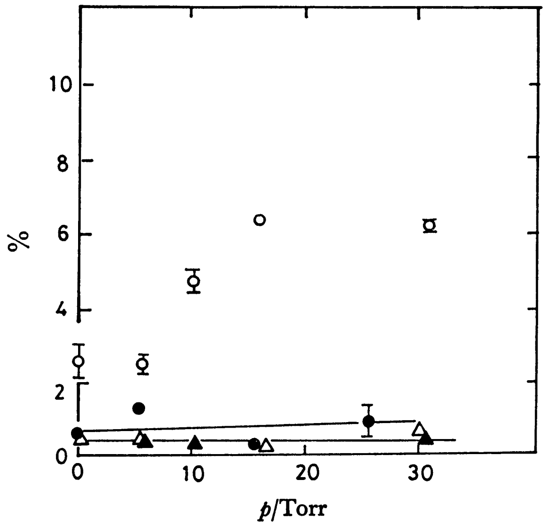

Fig. 3. Plots of the yield of ethanethiol and dimethyl sulfide as a function of the pressure of added methanethiol.
○: Ethanethiol in the absence of O_2, ●: ethanethiol in the presence of *ca.* 20 Torr O_2, △: dimethyl sulfide in the absence of O_2, ▲: dimethyl sulfide in the presence of *ca.* 20 Torr O_2.

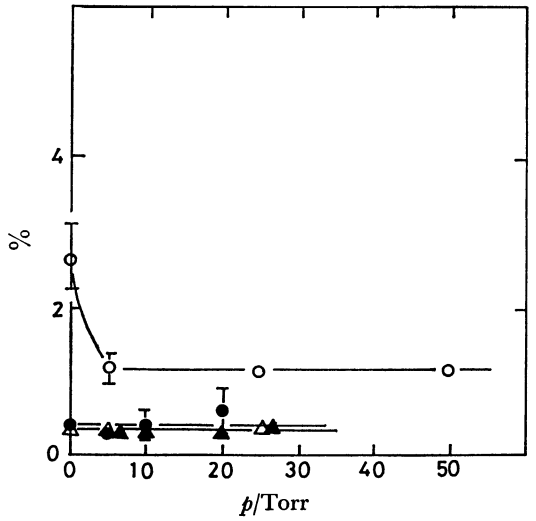

Fig. 4. Plots of the yield of ethanethiol and dimethyl sulfide as a function of the pressure of added hydrogen sulfide.
○: Ethanethiol in the absence of O_2, ●: ethanethiol in the presence of *ca.* 20 Torr O_2, △: dimethyl sulfide in the absence of O_2, ▲: dimethyl sulfide in the presence of *ca.* 20 Torr O_2.

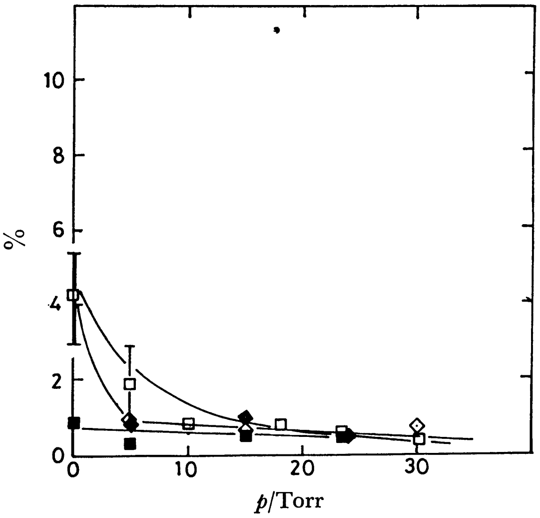

Fig. 5. Plots of the yield of diethyl sulfide as a function of the pressure of added methanethiol and added ethanethiol in the presence or in the absence of *ca.* 20 Torr O_2.
◇: Diethyl sulfide in the presence of methanethiol and in the absence of O_2, ◆: diethyl sulfide in the presence of methanethiol and in the presence of *ca.* 20 Torr O_2, □: diethyl sulfide in the presence of ethanethiol and in the absence of O_2, ■: Diethyl sulfide in the presence of ethanethiol and in the presence of *ca.* 20 Torr O_2.

indicates that there are other thermal processes involved in the formation of ethanethiol. One of these processes may be the hydrogen exchange of $C_2H_5{}^{35}S\cdot$ species with the added thiols. The radioactive ethylthio radical may react with ethanethiol to give radioactive ethanethiol, as in (1); it also reacts with methanethiol to give the ethanethiol, as in (2), by almost the same S–H bond dissociation energy as that of ethanethiol, as is shown in Fig. 3.

$$C_2H_5{}^{35}S\cdot + C_2H_5SH \longrightarrow C_2H_5{}^{35}SH + C_2H_5S\cdot \quad (1)$$

$$C_2H_5{}^{35}S\cdot + CH_3SH \longrightarrow C_2H_5{}^{35}SH + CH_3S\cdot \quad (2)$$

However it does not react with hydrogen sulfide by means of a higher S–H bond dissociation energy than that of the thiols ($\Delta D = 17.7$ kJ mol^{-1}).[20]

Figure 4 shows the decrease in the ethanethiol yield as the hydrogen sulfide is increased. The existence of the ethylthio radical is also supported by the following experimental fact.

The yield of diethyl sulfide decreases drastically in the presence of ethanethiol and methanethiol as is shown in Fig. 5.

The formation mechanism of this sulfide may be mainly considered to be the combination of ethylthio and ethyl radicals, because the yield of the sulfide was very much affected by the radical scavenger. The addition of the thiol may reduce the yield of the sulfide by the hydrogen donation. Accordingly, the existence of the ethylthio radical in the reaction system is confirmed by the above experimental findings but it can not become the precursor of ethanethiol without the help of the thiol additives. On the other hand, the radiochemical yield of dimethyl sulfide was not affected both in the presence and in the absence of the added dimethyl sulfide carrier.

The dimethyl sulfide thus does not seem to react with the radicals and the fragments formed in the reaction system.

The Effects of Carbonyl Sulfide and the Spin State of the Sulfur Atoms. The electronic states of the sulfur atoms produced by the nuclear transformation are not known. At a high initial recoil energy, many higher electronic states and S^{n+} ions may be possible. However, the sulfur in the higher excited states and in the ionic states may be quickly deactivated to the lowest electronic states by elastic and non-elastic collisions with its surroundings, and then chemical reactions may occur. These states are $^3P_2$ (ground state (0.00 kJ mol^{-1}), $^3P_1$ (4.76 kJ mol^{-1}), $^3P_0$ (6.85 kJ mol^{-1}), $^1D_2$ (110.46 kJ mol^{-1}) and $^1S_0$ (265.22 kJ mol^{-1}).[4] Although some differences in reactivity may exist in the three triplet states, it may be difficult to discriminate among them by usual chemical means.

For convenience, the sulfur atoms will be considered simply to have a ^3P ground-state and the two excited singlet-states, which are both metastable with transitions among them.[4]

Strausz and Gunning have proposed the following reaction schemes for the sulfur atoms produced by the photolysis of COS with hydrocarbons:[4]

$$\mathrm{COS} \xrightarrow{h\nu} \mathrm{S(^1D)} + \mathrm{CO} \tag{3}$$

$$\mathrm{S(^1D)} + \mathrm{RH} \begin{array}{l} \nearrow \mathrm{RSH} \quad (4a) \\ \searrow \mathrm{S(^3P)} + \mathrm{RH} \quad (4b) \end{array}$$

$$\mathrm{S(^1D)} + \mathrm{COS} \begin{array}{l} \nearrow \mathrm{S_2} + \mathrm{CO} \quad (5a) \\ \searrow \mathrm{S(^3P)} + \mathrm{COS^*} \quad (5b) \end{array}$$

$$\mathrm{S(^3P)} + \mathrm{COS} \longrightarrow \mathrm{S_2} + \mathrm{CO} \tag{6}$$

$$\mathrm{S(^3P)} + \mathrm{S(^3P)} \longrightarrow \mathrm{S_2} \tag{7}$$

$$\mathrm{S(^3P)} + \mathrm{S(^3P)} + \mathrm{M} \longrightarrow \mathrm{S_2} + \mathrm{M} \tag{8}$$

$$n\mathrm{S_2} \longrightarrow \mathrm{S}_{2n} \tag{9}$$

The rate constants of several steps have been reported: $k_{4a}=5\times10^7\ \mathrm{M^{-1}\ s^{-1}}$,[21] $k_{5a}\geqslant4\times10^{10}\ \mathrm{M^{-1}\ s^{-1}}$,[22] and $k_6=1.8\times10^6\ \mathrm{M^{-1}\ s^{-1}}$,[23] then, the disappearance of the S(^{1}D) atoms is about 1000 times greater than that of the corresponding thiol formation. In the ^{35}Cl(n,p)^{35}S reaction, the sulfur atoms produced are carrier-free, so the sulfur-sulfur combination reaction is improbable. Therefore, Schemes 7, 8, and 9 can be excluded.

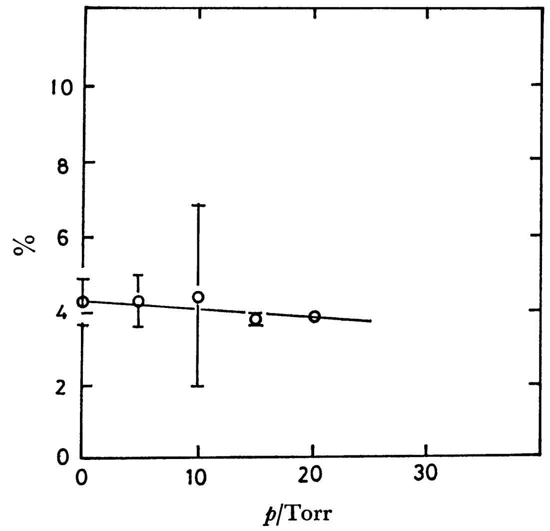

Fig. 6. Plots of the yield of ethanethiol as a function of COS pressure in the presence of 10 Torr ethanethiol.
The plots were corrected for the yield of ethanethiol-^{35}S in the collisional exchange reaction by the addition of 10 Torr ethanethiol as a protecting agent.

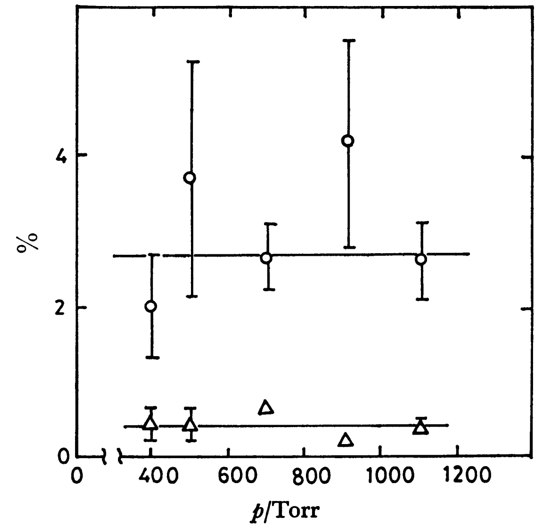

Fig. 7. Plots of the yield of ethanethiol and dimethyl sulfide as a function of total pressure.
○: Ethanethiol, △: dimethyl sulfide.

The radiochemical yield of ethanethiol in the reaction of sulfur atoms with ethane in the presence of COS is shown in Fig. 6. The yield of ethanethiol is 0.4% for an energetic reaction and 3.3% for a thermal reaction, as has been mentioned above. Therefore, the formation of ethanethiol proceeds mostly by means of a thermal process. The electronic states of the sulfur atoms for the formation of ethanethiol may be considered to be those of thermal sulfur atoms. The formation of ethanethiol was not affected by the addition of COS, and the yield kept constant. Such a constancy of the yield may imply that the contribution of S(^{1}D) atoms to the formation of ethanethiol is negligible in the thermal process.

Moreover, the formation of ethanethiol was not affected with the variation of the reaction pressure from 400 Torr to 1100 Torr, as is shown in Fig. 7. Strausz and Gunning have shown that the deactivation of the S(^{1}D) state to the S(^{3}P) state increases when the pressure of the reaction system is increased (300—2000 Torr).[4]

The yield of ethanethiol was reduced from about 2.6% to 1.1% by the addition of a small amount of ethylene. Davis and his coworkers have reported that ethylene reacts fast with the S(^{3}P) atoms (rate constant, 5×10^8 M^{-1} s^{-1}).[13] Also, thermochemically, the insertion reaction of the S(^{3}P) atoms into the C–H bond of ethane is 231.8 kJ mol^{-1} exothermic.

From the above facts and the thermochemical calculation, the insertion of S(^{3}P) atoms into the C–H bond may be possible, although the S(^{3}P) atoms must be accompanied by a spin conversion in the formation of the C–^{35}S–H bond.

Church and Rowland[3] have also reported that the S(^{3}P) atoms can be inserted into the secondary C–H bond of propane in the presence of a large amount of argon as a moderator.

Furthermore, Ring and Rabinovitch[25,26] have reported that the reaction of the triplet CH$_2$ (a diradical) produced by the photolysis of diazomethane in a large excess of inert N$_2$ can be inserted into the C–H bond of propane and isobutane in the gas phase. On the other hand, Gunning and his co-workers have concluded that the S(^{3}P) atoms do not insert into the C–H bond of hydrocarbons in the photolysis of COS; they concluded this from the marked decrease in the thiol yield in the presence of a large amount of CO$_2$.[4] This discrepancy can not be explained clearly, but it may presumably be expected that, in this system, a small yield of a sulfur compound is detectable, even if the reaction rate of the insertion by the S(^{3}P) is extremely slow as compared with that of the S(^{1}D) atoms; a small excess of the translational energy in this thermal reaction may then cause the insertion, even in the S(^{3}P) states.

The Ratio of the C–H and C–C Insertions. The insertion yield of the C–H bond in ethane is about 0.4% as an energetic process, and about 3.3% as a thermal process and the insertion yield of the C–C bond is about 0.3% as an energetic process.

Therefore the ratio of the rate constant in the energetic reaction can be represented as the ratio of the yields per bond, *i.e.*, (0.4/6)/0.3. The insertion into the C–C bond is about 5 times faster than that of the C–H insertion in the energetic process. In a previous paper,[5] it was pointed out that the insertion rate of the 2-position of the C–H bond in benzothiazole to that of the C–C bond in 2-methylbenzothiazole was slightly larger in the C–H bond.

In general, the insertion reaction of diradical into the C–H bond always takes place more easily in a weaker bond than a strong bond. For instance, the insertion rate in the reaction of CH$_2$, generated from the photolysis of diazomethane, into the primary C–H bond relative to that of the secondary in the propane molecule is 1:1.22.[27] The bond dissociation energy is 410.0 kJ mol^{-1} for the primary C–H bond and 395.4 kJ mol^{-1} for the secondary C–H bond in the propane molecule.[28]

Even in the energetic reaction, a similar fact was shown by Church and Rowland,[3] they concluded that the recoil sulfur atoms are inserted predominantly into the secondary C–H bond rather than the primary C–H bond in propane.

Moreover, it has been reported that the formation of the tritiated hydrogen (abstraction reaction) is reduced as the bond dissociation energy of hydrocarbons becomes greater.[29]

The above insertion and abstraction reactions are discussed in just the C–H bond in both the thermal and energetic processes. In the energetic reaction, it may be considered that the insertion reaction occurs also in the C–C bond, and a comparison of the insertion rate into the C–H bond with that of the C–C bond seems to show that it is also affected by the bond-dissociation energy. The bond-dissociation energy of the C–C bond is smaller than that of the C–H bond by about 41.8 kJ mol^{-1} in ethane.[28]

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