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Reaction of Recoil ^{35}S Atoms with Organic Compounds. Insertion Reaction of Recoil ^{35}S Atoms into the C-H and the C-C Bond

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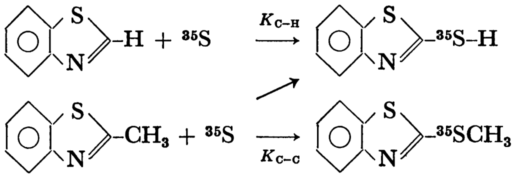
The insertion reactions of recoil sulfur atoms produced by the nuclear transformation of $^{35}Cl(n,p)^{35}S$ process into the C–H bond of benzothiazole and the C–C bond of 2-methylbenzothiazole have been examined. It has been found that the C–H insertion is a little easier than the C–C insertion by the energetic sulfur atoms, and that in thermal reaction the water used as a solvent seems to have some role in producing the C–H insertion product.

Sulfur atoms generated by the photolysis of COS react with organic compounds to produce insertion and addition products to the C–H and the C=C double bonds, such as the reaction of CH_2, oxygen and other carbenes.[1–4)]

Church and Rowland[5)] have studied the insertion reaction of recoil sulfur atoms into the primary and the secondary C–H bond in propane molecule to determine the spin states of the recoil sulfur atoms, and they have found that the sulfur atoms in the triplet state have inserted mainly into the secondary C–H bond. However, the insertion of diradicals into the C–C bond has not been reported.

In this study, the possibility of the insertion of recoil sulfur atoms produced by the nuclear transformation of $^{35}Cl(n, p)^{35}S$ process into the C–C bond was examined, with the aim of determining, if possible, the ratio of the insertion rate of the C–H bond to the C–C bond.

For the C–H and C–C bonds, the 2-position bond of benzothiazole (C–H compound) and the 2-position bond of 2-methylbenzothiazole (C–C compound) were respectively used. The insertion product of ^{35}S atoms to the 2-position of benzothiazole as in (1) leads to 2-mercaptobenzothiazole and to the 2-position of 2-methylbenzothiazole as in (2) leads to 2-(methylthio)benzothiazole. These compounds are well-known and stable substances.



(1)

(2)

Experimental

Materials. After the vacuum distillation of bezothiazole and 2-methylbenzothiazole (Tokyo Kasei Co.), hydrochloric acid was added. Then the hydrochlorides thus produced were purified by sublimation for benzothiazole and by recrystallization for 2-methylbenzothiazole. These starting materials were used as either an aqueous solution or a solid. Oxygen and nitrogen oxide (Takachiho Chem. Co.) were used as additives without further purification.

Thermal Neutron Irradiation. Thermal neutron irradiation of the starting material was performed in a quartz ampoule (about 0.5 ml) at a neutron flux of 3×10^{13} or 7×10^{13} n/cm²/s for 20 min with JRR-2 or JRR-3 of the Japan Atomic Energy Research Institute.

Separation, Purification, and Radioactivity Measurement of the Reaction Products. The separation and the purification were performed chromatographically and the radioactivity measurements of the products were carried out as previously described.[6)]

Nearly all the experimental data are averages of three runs; the errors are about 30% through all runs.

Results and Discussion

When the recoil sulfur atoms react with organic compounds, many reaction products labeled with ^{35}S may be produced by either the energetic process or the thermal one.[7)] In order to distinguish between the two processes, radical scavengers such as O_2 and NO are added to the sample; thus the thermal atoms and their reactions may be eliminated.[7)]

In this experiment, the total organic yield in aqueous solution was about 70%.[8)]

The Effect of Scavengers. From Tables 1 and 2, the yield of the C–^{35}S–H product from the C–H compound in the aqueous solution is clearly inhibited in the presence of NO or O_2. However, the yield of the C–^{35}S–C product from the C–C compound was not affected in the presence of the scavenger. From these results, it may be said that the C–H insertion takes place in both the thermal and energetic reaction, but the C–C insertion takes place only in the energetic reaction. This experi-

Table 1. Radiochemical yield of the C–^{35}S–H product from the C–H compound in the presence of scavengers in the aqueous solution

Concentration (weight %)		6.0			50.0					75.0	
Scavenger (Torr)	O_2	None			None	15	94	116	150	None	
	NO	None	10	300	None					None	51
Yield (%)		0.6	0.3	0.2	1.0	0.8	0.3	1.1[a)] 2.7[b)]	0.3	3.3	0.3

a) and b) show the yield obtained by the annealing after the thermal neutron irradiation. Annealing condition was at 95 °C for 1 h (a), or 120 °C for 1 h (b).

TABLE 2. RADIOCHEMICAL YIELD OF THE C-^{35}S-H AND THE C-^{35}S-C PRODUCT FROM THE C-C COMPOUND IN THE PRESENCE OF SCAVENGER AT THE CONCENTRATION OF 50%

Scavenger (Torr)	O_2	None	80	100	150
Yield (%)	C-^{35}S-H	0.6	0.3	—	0.3
	C-^{35}S-C	0.2	0.3	0.3	0.2

mental fact may not conflict with the results of the reactions of the carbenes produced by the photochemical and thermal processes.[1,2]

The Effect of Solvents and Their Concentrations. The yield of the C-^{35}S-C from the C-C compound shows a constant value in various concentrations of the aqueous solution and the solid. On the other hand, the yields of the C-^{35}S-H product from the C-H and the C-C compounds are affected by the concentration of the aqueous solution, as shown in Fig. 1. But in the presence of scavengers, the yield is no longer affected by the solution concentration. Higher concentration of the C-H compound give higher yields of the C-^{35}S-H product. However, the energetic reaction is not affected by the concentration of the C-H compound.

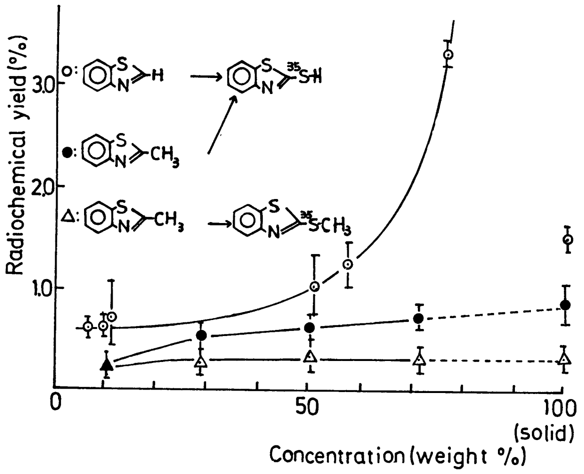


Fig. 1. Yields of the C-^{35}S-H and the C-^{35}S-C product from the C-H and the C-C compound in the aqueous solution.

Organic Solutions.[9] To elucidate the role of the solvent, various solvents such as methanol, benzene, and hexane were used. The results show that the yield of the C-^{35}S-H and the C-^{35}S-C were not affected in the presence of the scavenger nor by the variation of the concentration.

From these results, it seems that only the energetic reaction occurs in the organic solution; in this case thermal sulfur atoms may react easily with the organic solvent to give some other products.[3,4] Therefore, it is not suitable for the thermal reaction of recoil sulfur atoms to use the organic compounds as a solvent. Sulfur atoms seem to be more stable in water than the organic solutions.

The Annealing Effect on the Formation of the C-^{35}S-H Product.[10] After the neutron irradiation of the sample, the yield of the C-^{35}S-H products from the C-H compound in the aqueous solution increases by annealing. The result is shown in Table 1. Although the mechanism of this effect is not clear, it may be considered that the sulfur atoms give some other intermediate with the C-H compound or with water, and then it becomes the C-^{35}S-H product rather easily as a result of the annealing. It seems that the water plays some role in the reaction, because the annealing effect is found only in the aqueous solution and not in the organic solutions.

TABLE 3. RADIOCHEMICAL YIELDS OF THE C-^{35}S-C AND THE C-^{35}S-H PRODUCTS FROM THE C-C AND THE C-H COMPOUND IN VARIOUS ORGANIC SOLUTIONS

Solvent	Concentration (wt %)	Scavenger NO (Torr)	Yield (%) C-^{35}S-C product
Benzene	9.0	None	0.3
	51.0	None	0.3
	74.0	None	0.2

Solvent	Concentration (wt %)	Scavenger NO (Torr)	Yield (%) C-^{35}S-H product
Benzene	17.0	None	0.5
	38.0	None	0.4
	79.0	None	0.5
Hexane	61.0	None	0.3
		85	0.3
Methanol	32.0	None	0.2
		16	0.3
		180	0.2

p-Dichlorobenzene was used as a chlorine source of the nuclear transformation in these organic systems.

The Radiation Effect on the Formation of the Products. Thiols are easily decomposed by the radicals induced by radiation in aqueous solution, as follows:[11]

$$H_2O \rightsquigarrow H + OH \tag{3}$$

$$\text{R-SH} + OH \longrightarrow \text{RS} + H_2O \tag{4}$$

$$\text{R-SH} + H \longrightarrow \text{RS} + H_2 \tag{5}$$

The contribution of radiation to the formation and the decomposition of the product during the thermal neutron irradiation could not be estimated exactly. But from the comparison of the rate constant for the decomposition (k_6)[12] with that for the formation (k_7)[13] and the comparison of the number of the sulfur atoms produced $(8\times10^{12}$ atoms) by the nuclear transformation with the number of the hydrogen and hydroxyl radicals $(4\times10^{19}$ species)[14] formed, the insertion product may quite influenced by the radiation.[15]

$$\text{R-H} + S \xrightarrow{k_6} \text{R-SH} \tag{6}$$

$$\text{R-SH} + H \text{ and } OH \xrightarrow{k_7} \text{decomp} \tag{7}$$

The rate of the R-SH formation may be roughly estimated as the difference of reactions 6 and 7 by the following equation: $d[\text{R-SH}]/dt = k_6[\text{R-H}][S] - k_7[\text{R-SH}][H \text{ and } OH]$

The ratio of the rate constant of the decomposition to that of the formation (k_7/k_6) is about 10^4.

So, if the radiation effect can be neglected, the yield of the C-^{35}S-H compound in the reaction of the recoil sulfur atoms may be about 10 times larger than the experimental results of the C–^{35}S–H yield. This assumption may be supported by the experimental result that the sulfur atoms produced by the photolysis of CO^{35}S reacted with the C–H compound in the aqueous solution to give about 13% insertion product, based on the carbon monoxide produced.

The Ratio of the Rate Constant for the C–H to the C–C Insertion. Because of the low conversion of the reaction product, it can be considered that the ratio of the rate constant for the C–H to the C–C insertion may be equal to the ratio of the C–^{35}S–H to the C–^{35}S–C product yield.

The ratio of the rate constant of insertion ($K_{\mathrm{C-H}}/K_{\mathrm{C-C}}$) is about 1.5 in the energetic process. There are direct and indirect insertion reactions in the reaction of recoil sulfur atoms. One of the indirect insertion reaction is the addition to the –N=C– double bond to form $-\mathrm{N}-\underset{\substack{| \\ \mathrm{S}\cdot}}{\mathrm{C}}-\mathrm{H}$ as described by Grovenstein.[16] The other is the formation of C–^{35}S· intermediate by the reaction of energetic sulfur atoms with the C–H compound; this intermediate abstracts hydrogen from the surrounding molecules to form the C–^{35}S–H product.

The evidence for this reaction is shown by the formation of the C–^{35}S–H product from the C–C compound, as is shown in Table 2 and Fig. 1. Moreover, the hydrogen dissociation in the aqueous solution may be concerned with the production of the C–^{35}S–H, because the yield shows a higher value at the concentration of 75% than that of the solid state. In the reaction of carbon atoms using accelerated ^{14}C^{+} ions with benzene, toluene and cycloheptatriene were formed as synthetic products.[17] It was assumed that the energetic methylene must be involved in this reaction and gives C–H and C–C insertion products. The C–H insertion yield is higher than the C–C insertion in their experiments.

However, the photolytically generated ^{14}CH$_2$ reacts with benzene to give toluene in which the methyl group is exclusively labeled (C–H insertion product).[18] And naturally it is possible that the relative populations of the spin states of the recoil sulfur atoms may decide the yield and radioactivity distribution of the insertion product.

From these considerations, it may be concluded that the formation of the C–^{35}S–C is a direct insertion, but the C–^{35}S–H formation involves both direct and indirect insertion.

The C–^{35}S–H product gives a slightly higher yield than the C–^{35}S–C in the aqueous solutions.

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8) This value was estimated from the inorganic yield (mainly SO_4^{2-}, about 30%).

9) In this case, free benzothiazole or 2-methylbenzothiazole and *p*-dichlorobenzene were used as chlorine source.

10) This experimental fact was found in the use of an impure quartz tube; it was estimated that the irradiation temperature rose up about 120 °C in this case.

11) J. E. Pecker, "The Chemistry of Thiol Groups," Wiley-Interscience, New York (1974), p. 481.

12) The rate constant of decomposition of various thiols by radicals induced by radiation is of the order of 10^{10} M^{-1} s^{-1}.[11]

13) The rate constant of the insertion into the C–H bond of sulfur atoms generated by the photolysis of COS is 5×10^{7} M^{-1} s^{-1} in liquid phase.[3]

14) During thermal neutron irradiation in the nuclear reactor, the radiation dose may not be less than 10^{6}rad. The *G*-value of hydrogen atoms and hydroxyl radical is 3.65 and 2.95 respectively in the acidic aqueous solution.[15]

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