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Reactions of Recoil ^{35}S Atoms with Organic Compounds. I. The Distribution of ^{35}S Atoms on Mercaptobenzothiazole

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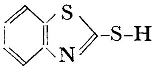
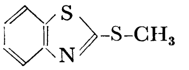
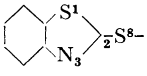
The reaction of ^{35}S atoms produced by neutron irradiation has been studied recently.[1,2] An appreciable proportion of the ^{35}S appears in oxidized forms,[3,4] especially as sulfate. Several investigations[5,6] have been reported regarding the chemical forms of ^{35}S, and extensive studies of the sulfur atom produced by the photolysis[7,8] of SCO have also been reported. However, few investigations[9] have been reported regarding the reaction of a sulfur atom produced by nuclear recoil reaction with organic compounds.

In this paper, the distribution of ^{35}S atoms in the molecules of mercaptobenzothiazole (I) and methylmercaptobenzothiazole (II) was studied; some differences in the reactions of the ^{35}S atoms formed by the ^{35}Cl(n,p)^{35}S and ^{34}S(n,γ)^{35}S processes were also investigated.


(I)


(II)

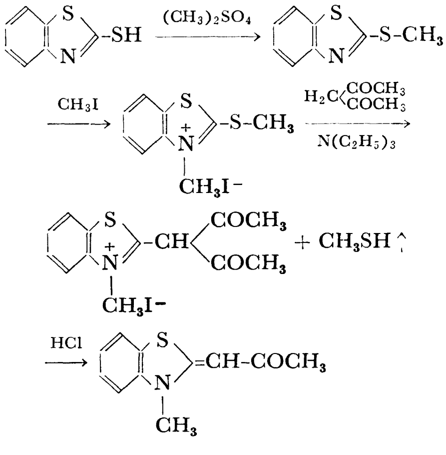


Experimental

Mercaptobenzothiazole (I) and methylmercaptobenzothiazole(II) (Tokyo Kasei Co.) were irradiated with JRR-1,2 and 3 reactors of the Japan Atomic Energy Research Institute in the absence of and in the presence of trichlorobenzene as a chlorine source. The irradiations were performed in a quartz ampule (0.5×3.0 cm) containing the sample.[*1]

Separation and Purification of an Irradiated Sample. For the degradation of an activated compound, the starting material (I and II) was added as a carrier to the irradiated sample; the purification was performed by recrystalization, reprecipitation, and solvent extraction.

Measurement of Radioactivity. All the samples were oxidized by the Shöniger[10] method or by the method using a Pirie reagent,[11] and the sulfate thus produced was precipitated by barium chloride. The activity of the barium sulfate thus obtained was measured at an infinite thickness by an end-window-type Geiger Müller counter. The specific activity of each compound was calculated from the saturation value of the apparent activity. The measurement of the total activity was carried out by the simultaneous irradiation of $(NH_4)_2SO_4$, NH_4Cl, and the targets. At each step of degradation of the sulfur compounds, the relative activity was measured. The degradation was performed by the following processes:[12]



Results and Discussion

As is listed in Table 1, the reactions of the ^{35}S atoms in the presence and in the absence of ben-

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1) C. Chiotan, I. Zamfir and M. Szabo, *J. Inorg. Nucl. Chem.*, **26**, 1132 (1964).

2) K. Yoshihara, Ting-Chia Huang, H. Ebihara and N. Shibata, *Radiochim. Acta*, **3**, 185 (1964).

3) J. Cifka and V. Bracokova, *J. Inorg. Nucl. Chem.*, **28**, 2483 (1966).

4) K. Taki and Y. Hishiki, *J. Phys. Chem. Inst.*, **37**, 106 (1961).

5) J. H. Freeman, M. Kasrai and A. G. Maddock, *Chem. Commun.*, **1967**, 979.

6) C. Chiotan, I. Zamfir and T. Costera, *J. Inorg. Nucl. Chem.*, **30**, 2857 (1968).

7) E. M. Lown, E. L. Dedio, O. P. Strausz and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 1056 (1967).

8) E. M. Lown, H. S. Sandhu, H. E. Gunning and O. P. Strausz, *ibid.*, **90**, 7164 (1968).

9) K. Taki, *J. Phys. Chem. Inst.*, **38**, 419 (1962).

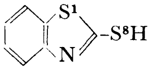
[*1] For the purpose of degassing, the sample was dissolved in pyridine or alcohol, and then the solvents were removed.

10) W. Schöniger, *Mikrochim. Acta*, **1956**, 869.

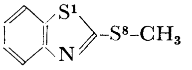
11) N. W. Pirie, *Biochem. J.*, **26**, 2041 (1932).

12) B. Beilenson and F. M. Hamer, *J. Chem. Soc.*, **1939**, 143.

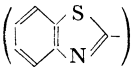
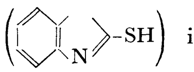
Table 1. Distribution (%) of ^{35}S produced by $^{35}Cl(n, p)^{35}S$ process in the presence and absence of benzoquinone

Benzoquinone %	 S$_1$-position	S$_8$-position
0	2.4	97.6
3.9	1.6	98.4

Mercaptobenzothiazole 0.2 g
1,2,4-Trichlorobenzene 0.1 g
Irradiation 2.5×10^{13} n/cm^2 sec, about 200 hr

Benzoquinone %	 S$_1$-position	S$_8$-position
0	2.2	97.8
3.5	5.7	94.3

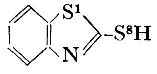
Methylmercaptobenzothiazole 0.4 g
1,2,4-Trichlorobenzene 0.1 g
Irradiation 2.5×10^{13} n/cm^2 sec, about 200 hr

zoquinone and oxygen as a radical scavenger[13] gave almost the same ^{35}S distribution. This experimental fact suggests that all the reactions may be considered to be hot reactions and not thermal reactions. The radiochemical yield of the activated parent molecule (retention value) is about 2—5% for the $^{35}Cl(n,p)^{35}S$ process and about 30% for the $^{34}S(n, \gamma)^{35}S$ process. The distribution of the ^{35}S atoms in the molecule is much greater in the S$_8$-position than in the S$_1$-position in both mercaptobenzothiazole (I) and methylmercaptobenzothiazole (II). The experimental results can not be reasonably interpreted, but it may be considered that the collisional exchange (a knock on exchange in terms of a billiard-ball model) of the sulfur atom is easier in the S$_8$-position than in the S$_1$-position in the molecule. By the collision of a hot atom, C–S–C bond rupture may occur in a moment. A large number of bond-cleaved intermediates may decompose, and some of them may combine in a short duration with slow-downed ^{35}S atoms which are located near the molecule. Therefore, the distribution of the ^{35}S atoms may be dependent on the stability of the bond-cleaved intermediate. It may be considered that the intermediate which is bond-cleaved at the S$_8$-position  is more stable than that at the S$_1$-position  in the mercaptobenzothiazole molecule.

Reaction of ^{35}S Atoms Formed by Two Nuclear Reactions. In the presence of trichlorobenzene, since the activation cross-section of ^{34}S and ^{35}Cl is almost the same (0.26 barn for ^{34}S and 0.17 barn for ^{35}Cl) and since the number of atoms of ^{35}Cl is much larger than that of ^{34}S, the $^{34}S(n, \gamma)^{35}S$ process can be disregarded. In this case the reactions are brought about by hot ^{35}S atoms produced by the $^{35}Cl(n, p)^{35}S$ process. On the other hand, in the absence of trichlorobenzene the reactions are brought about by hot ^{35}S atoms produced by the $^{34}S(n, \gamma)^{35}S$ process. The experimental results on hot ^{35}S atoms from the two formation processes are listed in Table 2. The ratio of ^{35}S atoms at the S$_8$-position to those at the S$_1$-position is smaller in the process of $^{34}S(n, \gamma)^{35}S$ than in that of the $^{35}Cl(n, p)^{35}S$ process in all the runs, as is shown in Table 2; the ^{35}S atoms formed from ^{34}S exchange with S$_8$-sulfur more easily than the ^{35}S atoms formed from ^{35}Cl.

The chemical reaction may occur when hot atoms have been slowed[14] sufficiently (25 eV—50 eV).

Table 2. Distribution (%) of ^{35}S produced by $^{34}S(n, \gamma)^{35}S$ and $^{35}Cl(n, p)^{35}S$ process

Process	 S$_1$-position	S$_8$-position	$\frac{S_8}{S_1}$	(Retention value) yield %
$^{34}S(n, \gamma)^{35}S$	12.6	87.4	6.9	27.5
$^{35}Cl(n, p)^{35}S$	5.4	94.6	17.5	4.8

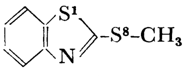
Cl source: p-Dichlorobenzene (^{35}Cl atoms/^{34}S atoms = 10)

Irradiation 3×10^{11} n/cm^2 sec, 240 hr
Targets were not degassed.

Process	S$_1$-position	S$_8$-position	$\frac{S_8}{S_1}$	(Retention value) yield %
$^{34}S(n, \gamma)^{35}S$	6.4	93.6	14.6	
$^{35}Cl(n, p)^{35}S$	3.6	96.4	26.8	

Cl source: Trichlorobenzene (^{35}Cl atoms/^{34}S atoms = 11

Irradiation 4×10^{13} n/cm^2 sec, 144 hr

Process	 S$_1$-position	S$_8$-position	$\frac{S_8}{S_1}$	(Retention value) yield %
$^{34}S(n, \gamma)^{35}S$	12.5	87.5	7.0	
$^{35}Cl(n, p)^{35}S$	7.1	92.9	13.1	

Cl source; Trichlorobenzene (^{35}Cl atoms/^{34}S atoms = 10)

Irradiation 4×10^{13} n/cm^2 sec, 200 hr

Process	S$_1$-position	S$_8$-position	$\frac{S_8}{S_1}$	(Retention value) yield %
$^{34}S(n, \gamma)^{35}S$	17.1	82.9	4.8	29.7
$^{35}Cl(n, p)^{35}S$	10.5	89.5	8.5	2.1

Cl source: Trichlorobenzene (^{35}Cl atoms/^{34}S atoms = 20)

Irradiation 1×10^{11} n/cm^2 sec, 288 hr

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13) A. F. Trotman-Dickenson, "Free Radicals: An Introduction," Methuen & Co. Ltd., London (1959), p. 14

14) A. P. Wolf, C. S. Redvanly and R. C. Anderson, *J. Amer. Chem. Soc.*, **79**, 3717 (1957).

The reaction of sulfur atoms may not be affected by the initial recoil energy, about 17 keV for the $^{35}Cl(n, p)^{35}S$ process and about 1 keV for the $^{34}S(n, \gamma)^{35}S$ process, because the recoil energy is too high to react with an organic compound. Also, because of the simultaneous irradiation of the sample for two nuclear reactions, the effect of radiation damage may be disregarded.

It has been reported that, in the reaction of the ^{11}C formed from the $^{12}C(n, 2n)^{11}C$, $^{12}C(p, pn)^{11}C$,[15,16] and $^{12}C(\gamma, n)^{11}C$[17] processes, no essential differences are found among the processes.

The present author does not have any reasonable explanation for the experimental facts. It may, however, be presumably postulated that the distribution of ^{35}S atoms is affected by the original position of the nuclear-transformed atom in the molecule.

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15) G. Stöcklin H. Stangl, D. R. Christman, J. B. Cumming and A. P. Wolf, *J. Phys. Chem.*, **67**, 1735 (1963).

16) G. Stöcklin and A. P. Wolf, *J. Amer. Chem. Soc.*, **85**, 229 (1963).

17) MacKay and R. Wolfgang, *ibid.*, **83**, 2399 (1961).