chromatography. The structure of **7a**, mp 148–148.5°, [α]D +22.8° ($CHCl_3$), was established by comparison with a sample synthesized by oxidation of **6a** with *m*-chloroperbenzoic acid. The second product, mp 147–148°, was assigned structure **9a** from spectral data; this was substantiated by an independent synthesis from **10a**[7] by *m*-chloroperbenzoic acid oxidation. It is obvious that compound **7a** is formed by a nucleophilic attack of the C-3 carbanion on the 2β-bromomethyl group, while formation of compound **9a** can be accounted for by the arrows shown in structure **8**, i.e., a rearrangement initiated by formation of the C-6 carbanion.

Cyclization leading to **7a** was best achieved under the following optimum conditions. Namely, treatment of **8a** (Y = Br) with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in DMF at −30° for 1 hr gave **7a** in 80% yield. Similarly, sulfoxide **8c** (Y = Br) derived from **8a** (Y = Br) by a deacylation method[8] gave **7c**, tosylate mp 176–179° dec, in 81% yield. These results indicate that the intramolecular cyclization proceeds faster than the intramolecular rearrangement and also suggest that cyclization of **4a** (Y = Br) would take place preferentially without production of the episulfonium ion **3** if a strong base was employed.

This was corroborated as follows. Treatment of **4a** with DBU under the conditions as described above yielded **6a** in ca. 80% yield; however, this reaction was always accompanied by production of the undesired cephem **11a**, 8%. Tricyclic sulfide **6a** was also derived from **7a** by reduction with PCl_3 in DMF in 76% yield. The synthesis of **6a** from **4a** represents the first intramolecular nucleophilic displacement in the penam system.[9,10]

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(10) Conversion of compound **6** to 2-methylcephem will be reported shortly.

Takashi Kamiya,* Tsutomu Teraji, Masashi Hashimoto
Osamu Nakaguchi, Teruo Oku
Research Laboratories, Fujisawa Pharmaceutical Co., Ltd.
Osaka 532, Japan

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Evidence for $S(^1D)$ Atom Reactions Involving $^{34}S(n,\gamma)^{35}S$ Nuclear Recoil Generated Sulfur

Sir:

Reactions of recoil sulfur atoms produced by both the $^{35}Cl(n,p)^{35}S$ and $^{34}S(n,\gamma)^{35}S$ nuclear processes in the gas phase are known to be quite complex[1] due primarily to the polyvalent nature of the atom. In addition the propensity for sulfur species to undergo oxidation reduction processes further complicates the identification and characterization of primary reaction channels. Earlier accounts of nuclear recoil sulfur reactions have, in general, ignored the role of electronic excitation, or, as reported in one case, the contribution of $S(^1D)$ has been discounted as being unimportant.[2]

Table I. Data for $^{35}S + CS_2$ Exchange Reaction as a Function of Gaseous Additives

Additives		Sample composition (Torr)			Yield $CS^{35}S$ normalized activity[a]
M	N	P_{CS_2}	P_M	P_N	
		200			490 ± 10
H_2		200	100		350 ± 10
H_2		200	200		256 ± 10
H_2		200	400		153 ± 5
H_2	Ar	200	100	1077	235 ± 10
C_2H_6		200	400		49 ± 3
C_2H_4		200	400		41 ± 2

[a] The yield of $CS^{35}S$ is the normalized activity per Torr of S available. Results reported are the average of two or more determinations and the errors are based upon the statistical errors in the aliquots counted.

The differences in reactivity for the low lying electronic states of sulfur atoms have been extensively characterized in systems where the atoms are photochemically generated.[3] In particular, changes in both reaction mechanisms and reaction rates are known to be associated with $S(^1D)$ and $S(^3P)$ reactions. Direct use of the techniques employed in photochemical systems, however, has not led to an unambiguous interpretation of nuclear recoil systems.[2] We have obtained evidence for the gas phase reactions of singlet sulfur atoms, $S(^1D)$, generated by the $^{34}S(n,\gamma)^{35}S$ nuclear recoil reaction in the presence of CS_2.

The recoil sulfur species were generated by thermal neutron irradiation for 10 min to 1 hr at a flux of 10^{12} (n/cm^2)/sec on a rotating multiple sample holder at the Washington State Nuclear Radiation Center. All samples were prepared by standard high vacuum techniques and flame sealed in 15-cm^3 cylindrical quartz irradiation vessels. Carbon disulfide (Matheson Coleman and Bell) was thoroughly degassed and vacuum distilled before use. No impurities were detected by gas chromatography. Research grade C_2H_4 and C_2H_6 (Phillips) and H_2 and Ar (Matheson) additives were used directly from gas cylinders. Product analysis was carried out by radio gas chromatography incorporating an internal flow proportional detector.

The reactions between both triplet and singlet sulfur atoms and CS_2 are known to occur in the gas phase and have been discussed previously.[4] In this study the effect of various gas additives on the total production of $CS^{35}S$ from nonlabeled CS_2 has been determined in order to investigate the role of various forms of recoil atom excitation in driving the exchange reaction. In Table I, the $CS^{35}S$ produced as a function of H_2 dilution and at fixed dilution with C_2H_4, C_2H_6, and Ar is tabulated. The activity of the labeled CS_2 is reported as specific activity per Torr of CS_2 originally present in the sample mixture.[5]

The results indicate that the efficiency of the sulfur atom exchange reaction with CS_2 rises linearly within experimental error as the mole fraction of CS_2 increases. This behavior suggests that the hydrogen additive is competing effectively for the reactive sulfur atoms or sulfur containing intermediates.[6] Such competition might arise from a moderating effect on a hot reaction, an exchange reaction between an excited intermediate and CS_2, or a quenching effect which eliminates electronically excited states of atomic sulfur. The reaction of ground electronic state sulfur atoms with H_2, if it occurs at all, cannot compete with the reaction of $S(^3P)$ with CS_2 in this system unless the sulfur has excess translational energy.[7,8] The existence of a reactive intermediate cannot be ruled out, but it seems unlikely that any chemically realistic intermediate, except CS_3^*, which yields labeled CS_2 would react competitively with H_2.[9] Excited CS_3^* if formed might undergo exchange reaction with CS_2 or be stabilized by collision with bath gas as discussed below.

To distinguish between these mechanistic routes to labeled CS_2, a large excess of Ar was added to a 2 to 1 mixture of CS_2 and H_2 as shown in Table I. Argon is reported to have a very small quenching rate constant for $S(^1D)$ compared with H_2 and hydrocarbons and, therefore, it should not markedly affect the distribution of $S(^1D)$ to $S(^3P)$ atoms even at relatively high dilution.[3] It is, however, known to be a reasonably good hot atom moderator and is also expected to be as good an energy transfer agent as H_2 in stabilizing any excited CS_3^* present. The small decrease in labeled CS_2 product observed at high dilution with Ar is not consistent either with a model based primarily upon a translationally hot process or one in which exchange reaction between CS_3^* and CS_2 is dominant. In fact the contribution from the latter process is estimated to be less than 5% on the basis of these data.

The most reasonable reaction mechanism which accounts for the major features of the data is based upon excited singlet sulfur atom exchange reactions with CS_2 in competition with quenching as indicated in the following scheme.

$$S(^1D) + CS_2 \xrightarrow{k_1} CS_2\text{ (labeled)} \tag{1}$$

$$S(^1D) + M \xrightarrow{k_2} S(^3P)\text{ or MS} \tag{2}$$

$$S(^3P) + CS_2 \xrightarrow{k_3} CS_3^* \xrightarrow{CS_2\text{ or M}} CS_3 \longrightarrow \text{wall} \tag{3}$$

Chemically activated CS_3^* postulated in reaction 3 is not expected to competitively decompose at pressures of 200 Torr and greater.[4] This set of reactions can be treated quantitatively in a manner similar to that reported by Donovan et al.[10] in quenching studies of $S(^1D)$. The fraction of $S(^1D)$ which gives labeled CS_2 in experiments containing CS_2 reactant and additive M is equal to $k_1[CS_2]/(k_1[CS_2] + k_2[M] + T)$ where T represents the rate of removal of $S(^1D)$ by all additional reaction channels. If T and $[CS_2]$ are constant, a plot of the reciprocal of the CS_2 activity as a function of additive [M] should yield a straight line whose slope is proportional to $k_2/k_1[CS_2]$. The reciprocal of the CS_2 activity as a function of H_2 additive shown in Table I was fitted by a linear least-squares procedure giving a correlation coefficient of 0.995. The resulting linear behavior indicates that the data are consistent with the mechanism involving $S(^1D)$ exchange reaction with CS_2.

This evidence for the existence of singlet sulfur atom reactions in no way excludes the possibility of concurrent triplet sulfur atom reactions, and indeed triplet sulfur atoms are expected to be present both as hot and thermalized species. The fact that they presumably do not play a significant role in yielding labeled CS_2 despite reports that triplet sulfur reacts with carbon disulfide is consistent with the formation of the relatively stable intermediate CS_3 postulated by Breckenridge and Taube.[4] Since the probability of a collision between this intermediate and either another CS_3 species or sulfur on the walls is vanishingly small in this system, the postulated decomposition to give labeled CS_2 is not important and any labeled CS_3 formed is expected to be lost to the quartz surfaces of the reaction vessel as indicated by reaction 3. Other mechanisms for removal of $S(^3P)$ atoms are also possible, of course, but there is no evidence that they contribute significantly to the carbon disulfide product observed.

C_2H_6 and C_2H_4 additives were also used to distinguish between triplet and singlet reactions as shown in Table I.[11] In both cases the yield of labeled CS_2 was significantly depressed in a reaction system consisting of CS_2 and hydrocarbon in a ratio of 1:2. Reaction and quenching of singlet sulfur by both C_2H_6 and C_2H_4 are known to be efficient whereas reaction of triplet sulfur is known to occur readily only with ethylene.[3b,c]

It appears then that there is clear evidence for the presence and reaction of $S(^1D)$ atoms in this nuclear recoil reaction system incorporating the $^{34}S(n,\gamma)^{35}S$ process. It is also probable that $S(^1D)$ reactions have played an important role in earlier reports of recoil sulfur atom reactions and are responsible for the complexity observed due to the large number of reaction paths available.

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(12) Camille and Henry Dreyfus Teacher-Scholar, 1971–1976.

L. N. Kremer, Leonard D. Spicer*[12]
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received November 23, 1974

Synthesis and Cryptate Complexes of a Spheroidal Macrotricyclic Ligand with Octahedrotetrahedral Coordination[1]

Sir:

The molecular recognition of the spherical alkali and alkaline earth cations by an organic ligand should be ideally achieved by a system containing a spherical intramolecular cavity into which the cation may be included. Macrocyclic systems define a circular cavity and macrobicyclic ligands an ellipsoidal one. In an analysis of the features of polycyclic ligands,[2] a spheroidal macrotricyclic system (see type I