

chromatography. The structure of **7a**, mp 148–148.5°, [α]D +22.8° (CHCl₃), 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, sulfide **8c** (Y = Br) derived from **8a** (Y = Br) by a deacylation method⁸ 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 PCl₃ 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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References and Notes

- (1) Studies on β-lactam antibiotics. II. Part I, ref 2.
- (2) T. Kamiya, T. Teraji, Y. Saito, M. Hashimoto, O. Nakaguchi, and T. Oku, *Tetrahedron Lett.*, 3001 (1973).
- (3) T. Kamiya, T. Teraji, M. Hashimoto, O. Nakaguchi, and T. Oku, in preparation.
- (4) Details of preparations, characterizations, and antimicrobial activities will be dealt with in a forthcoming publication.
- (5) R. D. G. Cooper, L. D. Hatfield, D. O. Spry, *Acc. Chem. Res.*, **6**, 32 (1973), and references therein.
- (6) S. Kukulja and S. R. Lammert, *J. Am. Chem. Soc.*, **94**, 7169 (1972).
- (7) Compound **10a**, mp 208–209°, was obtained by the procedure described in R. B. Morin, B. G. Jackson, R. A. Muller, E. R. Labogno, W. B. Scanlon, and S. L. Andrews, *J. Am. Chem. Soc.*, **91**, 1401 (1969).
- (8) (a) B. Fechtig, H. Peter, H. Bickel, and E. Vischer, *Helv. Chim. Acta*, **51**, 1108 (1969); (b) F. M. Huber, R. R. Chauvette, and B. G. Jackson in "Cephalosporins and Penicillins: Chemistry and Biology", E. H. Flynn, Ed., Academic Press, New York, N.Y., 1972, Chapter 2.
- (9) A Series of 7-acyl derivatives (**6** (R₂ = H)) have been prepared. Biological tests show that these derivatives possess gram positive activity; however, they show reduced activity against gram negative bacteria.
- (10) Conversion of compound **6** to 2-methylcephem will be reported shortly.

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Evidence for S(¹D) Atom Reactions Involving ³⁴S(n,γ)³⁵S Nuclear Recoil Generated Sulfur

Sir:

Reactions of recoil sulfur atoms produced by both the ³⁵Cl(n,p)³⁵S and ³⁴S(n,γ)³⁵S nuclear processes in the gas phase are known to be quite complex¹ due primarily to the

Table I. Data for ³⁵S + CS₂ Exchange Reaction as a Function of Gaseous Additives

Additives	Sample composition (Torr)			Yield CS ³⁵ S normalized activity ^a
	M	N	P _{CS₂}	
			200	490 ± 10
H ₂			200	350 ± 10
H ₂		100	200	256 ± 10
H ₂		400	200	153 ± 5
H ₂	Ar	100	1077	235 ± 10
C ₂ H ₆		400	200	49 ± 3
C ₂ H ₄		400	200	41 ± 2

^a The yield of CS³⁵S 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.

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

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 ³⁴S(n,γ)³⁵S nuclear recoil reaction in the presence of CS₂.

The recoil sulfur species were generated by thermal neutron irradiation for 10 min to 1 hr at a flux of 10¹² (n/cm²)/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-cm³ 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 C₂H₄ and C₂H₆ (Phillips) and H₂ 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.

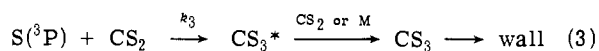
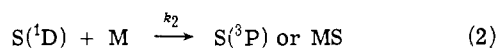
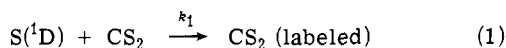
The reactions between both triplet and singlet sulfur atoms and CS₂ are known to occur in the gas phase and have been discussed previously.⁴ In this study the effect of various gas additives on the total production of CS³⁵S from nonlabeled CS₂ has been determined in order to investigate the role of various forms of recoil atom excitation in driving the exchange reaction. In Table I, the CS³⁵S produced as a function of H₂ dilution and at fixed dilution with C₂H₄, C₂H₆, and Ar is tabulated. The activity of the labeled CS₂ is reported as specific activity per Torr of CS₂ originally present in the sample mixture.⁵

The results indicate that the efficiency of the sulfur atom exchange reaction with CS₂ rises linearly within experimental error as the mole fraction of CS₂ 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 CS₂, or a quenching effect which eliminates electronically excited states of atomic sulfur. The reaction of ground electronic state sulfur atoms with H₂, if it occurs at all, cannot compete with the reaction

of S(³P) with CS₂ 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 CS₃^{*}, which yields labeled CS₂ would react competitively with H₂.⁹ Excited CS₃^{*} if formed might undergo exchange reaction with CS₂ or be stabilized by collision with bath gas as discussed below.

To distinguish between these mechanistic routes to labeled CS₂, a large excess of Ar was added to a 2 to 1 mixture of CS₂ and H₂ as shown in Table I. Argon is reported to have a very small quenching rate constant for S(¹D) compared with H₂ 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 H₂ in stabilizing any excited CS₃^{*} present. The small decrease in labeled CS₂ 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 CS₃^{*} and CS₂ 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 CS₂ in competition with quenching as indicated in the following scheme.



Chemically activated CS₃^{*} 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 CS₂ in experiments containing CS₂ 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 CS₂ 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 CS₂ activity as a function of H₂ 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 CS₂.

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 CS₂ despite reports that triplet sulfur reacts with carbon disulfide is consistent with the formation of the relatively stable intermediate CS₃ postulated by Breckenridge and Taube.⁴ Since the probability of a collision between this intermediate and either another CS₃ species or sulfur on the walls is vanishingly small in this system, the postulated decomposition to give labeled CS₂ is not important and any labeled CS₃ 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.

C₂H₆ and C₂H₄ additives were also used to distinguish between triplet and singlet reactions as shown in Table I.¹¹ In both cases the yield of labeled CS₂ was significantly depressed in a reaction system consisting of CS₂ and hydrocarbon in a ratio of 1:2. Reaction and quenching of singlet sulfur by both C₂H₆ and C₂H₄ 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 ³⁴S(n,γ)³⁵S 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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References and Notes

- (1) (a) M. L. Hyder and S. S. Markowitz, *J. Inorg. Nucl. Chem.*, **26**, 257 (1964); (b) K. Panek and K. Mudra, "Chemical Effects of Nuclear Transformations", Vol. 1 IAEA, Vienna, 1965, p 195; (c) E. K. C. Lee, Y. N. Tang, and F. S. Rowland, *J. Phys. Chem.*, **68**, 318 (1964).
- (2) L. B. Church and F. S. Rowland, *Radiochim. Acta*, **16**, 55 (1971).
- (3) (a) R. J. Donovan and D. Husain, *Chem. Rev.*, **70**, 489 (1970); (b) O. P. Strausz, "Organosulphur Chemistry", M. J. Janssen, Ed., Interscience, New York, N.Y., 1967; (c) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, **4**, 143 (1966).
- (4) W. H. Breckenridge and H. Taube, *J. Chem. Phys.*, **53**, 1750 (1970).
- (5) Activities reported in this way are directly proportional to the product yield under constant irradiation conditions. In these experiments the error in assuming uniform exposure is estimated to be 5%.
- (6) The possibility of a unimolecular decomposition route involving CS₂^{*} which is responsible for the major features of this reaction can be discounted on the basis of the observed decrease in labeled CS₂ with increased additive and concurrent increased pressure.
- (7) P. Fowles, M. deSorgo, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **89**, 1352 (1967).
- (8) The rate constant for the reaction of S(³P) with CS₂ at 25° is estimated to be $\sim 8.4 \times 10^{-13}$ cm³/(molecule sec) on the basis of ref 4 and the recent report by R. B. Klemm and D. D. Davis, *J. Phys. Chem.*, **78**, 1137 (1974).
- (9) This includes the possibility of a long-lived intermediate such as C³⁵S. (a) K. Schofield, *J. Phys. Chem. Ref. Data*, **2**, 25 (1973); (b) W. H. Breckenridge, private communication.
- (10) D. J. Little, A. Dalgleish, and R. J. Donovan, *Faraday Discuss. Chem. Soc.*, **53**, 211 (1972).
- (11) Recently separate experiments in this laboratory have indicated the formation of a sizable amount of ethyl mercaptan in the reaction between ethane and nuclear recoil sulfur atoms produced by the (n,p) process under conditions of 55% moderation. This result also strongly indicates the presence and reaction of S(¹D) atoms.
- (12) Camille and Henry Dreyfus Teacher-Scholar, 1971-1976.

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Synthesis and Cryptate Complexes of a Spheroidal Macrotricyclic Ligand with Octahedrotetrahedral Coordination¹

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