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CHEMICAL EFFECTS FOLLOWING THE $S^{34}(n,\gamma)S^{35}$ REACTION
IN GASEOUS-SULFUR COMPOUNDS^{*,†}

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August 1962

Abstract — The chemical behavior of S^{35} formed by the $S^{34}(n,\gamma)$ reaction has been studied in gaseous H_2S , SO_2 , SF_6 , CH_3SH , and thiophene. We obtained the reaction by sealing the gases in quartz ampules and irradiating them with thermal neutrons in the Livermore pool-type reactor (LPER). Among the effects studied were those of pressure, surface area, and additive gases including argon, nitric oxide, oxygen, and hydrogen. The S^{35} was recovered in gaseous compounds and in deposits on the walls of the ampules; the chemical composition of both portions of activity was determined by aqueous chemistry using carriers. The results are consistent with a model in which the original molecule is broken up in the recoil process and the resulting fragments containing S^{35} react with the surroundings only after they have slowed to thermal energies; in general, the final chemical form of the S^{35} is determined by the chemical environment in which it is produced rather than by its original oxidation state or chemical form. However, irradiations of mixtures of several gases with NO gave results possibly indicating that the chemical form of the S^{35} immediately after molecular disruption may depend upon the nature of the original molecule.

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INTRODUCTION

The study of the chemistry of radioactive products of nuclear reactions offers a unique tool for an examination of the chemical behavior of molecular fragments with high kinetic energy. The nuclear reaction imparts a high recoil momentum to the atom involved. This momentum may suffice to break the atom's chemical bonds and give it high kinetic energy as well, so that it recoils through its surroundings as a "hot" atom or ion. Following its subsequent chemical reaction, it can be identified by its radioactivity. A hot atom recoiling through a liquid or solid is restricted to a relatively small region by recoil from surrounding atoms, and when it is finally slowed to thermal energies it may react chemically with the excited chemical species produced in the slowing process. In the gas phase, however, the interval between collisions is so large that chemical reactions with the undisturbed surroundings are possible. Experimental systems of this type have been investigated by a number of authors who studied particularly the reactions of tritium with organic materials,⁽¹⁾ reactions of various halogens,^(2,3) and others.^(4,5) Estrup and Wolfgang⁽⁶⁾ have been able to characterize the reaction of tritium with methane to give CH_3T as being due to tritium atoms with kinetic energy above thermal energy. Gordus and Hsiung have further extended the theory and have given a theoretical treatment of the bond-breaking process.⁽⁷⁾

In our work the reactions of S^{35} produced by $\text{S}^{34}(\text{n},\gamma)$ were studied in a variety of gaseous systems. The reactions of S^{35} were first investigated by Levey, Milham, Rice, and Willard⁽⁸⁾ and have recently been studied by Herber, who reviews earlier work.⁽⁹⁾ In most of these experiments the S^{35} was produced in condensed systems by the $\text{Cl}^{35}(\text{n},\text{p})\text{S}^{35}$ reaction. It was felt that study of gas-phase reactions of S^{35} would help answer questions regarding oxidation or reduction resulting from the nuclear process, and might additionally indicate to what extent multiple bonds are broken.

The radioisotope S^{35} is formed from S^{34} , which is 4.2% abundant in natural sulfur,⁽¹⁰⁾ with a cross section which is 0.26b for thermal neutrons.⁽¹¹⁾ The half-life of S^{35} is 87 days, and it decays by emission of β^- particles with a maximum energy of 0.168 MeV. No gamma radiation accompanies decay.⁽¹⁰⁾

Experiments were carried out to determine the behavior of S^{35} formed from H_2S , SO_2 , SF_6 , CH_3SH , and thiophene. The gases were sealed into quartz ampules and irradiated with thermal neutrons in the thermal column of the LPTR; the activity found in the gas phase and that deposited on the walls were determined and chemically characterized by the use of carriers and aqueous chemistry. The reactions of S^{35} were studied at various pressures and with different amounts of surface area of the container. The effects of the addition of other gases, such as O_2 , NO , H_2 , and Ar , were determined in an effort to characterize the reaction mechanisms involved.

EXPERIMENTAL

Materials, irradiations, and counting

Most of the gases used were Matheson chemically pure grade. Thiophene was supplied by Eastman Organic Chemicals and methyl mercaptan was furnished by the chemicals division of the American Oil Company. All were used without further purification, except NO, which was distilled to remove other nitrogen oxides.

All samples were sealed into cylindrical quartz bulbs for irradiation. The bulbs, which had volumes of 3 to 10 cm³, were washed repeatedly with distilled water before use, and heated under vacuum with a torch immediately before filling, to remove as much volatile material as possible from the walls. For some studies, special bulbs were prepared which were packed with fine quartz wool. Measurements indicated that the total surface area of these fibers was 5 to 10 times that of the inside of the tube.

Irradiations were carried out in the West Thermal Facility of the LPTR at the Livermore site of the Lawrence Radiation Laboratory. Nominal neutron fluxes used were in the range of 1 to 5×10^{11} neutrons per cm² per sec, and the irradiation required approximately 16 hours. Attempts were made to ascertain the total amount of S³⁵ produced in each sample by determining the amount of Au¹⁹⁸ activity induced by the Au¹⁹⁷(n,γ) reaction in gold foils attached to the individual sample tubes. This activity was compared to that in a similar gold foil attached to a sample tube containing (NH₄)₂SO₄; the specific activity of S³⁵ produced in this sample was then determined, and the relative Au¹⁹⁸ activities were used to calculate the S³⁵ activity expected in the gaseous samples. It was found, however, that the variation of flux with position in the reactor was so severe that the activity induced in a given sample could not, in general, be accurately calculated in this manner. The difference between the calculated and

total recovered S^{35} activities was about $\pm 10\%$ in the most favorable irradiations but often reached or exceeded $\pm 50\%$ in others.

Tests were carried out to ascertain that the activity recovered was entirely S^{35} . The only contaminant found was 14-day P^{32} , presumably produced by the $S^{32}(n,p)$ reaction; this activity was never greater than 2% of the S^{35} activity.

The gross radiation level in the region of irradiation was estimated as about 5×10^5 r/h. It was calculated that radiation damage to the sample would be considerably less than 1%, and the quantitative recovery of the irradiated gas indicates that this was the case. Because the S^{35} is a trace species, the radiation products may be significant in the further reaction of the S^{35} .

No control over the temperature of the sample during irradiation was possible, but it is believed not to have exceeded 40°C , as the facility is water-cooled.

Ordinarily 10 to 20 tubes were irradiated simultaneously, and the analysis was carried out over a period of several months following irradiation. No effects dependent on the time between irradiation and analysis were noted.

The activity was ordinarily assayed in a chromium-lined proportional counter similar to that described by Wolfgang and McKay.⁽¹²⁾ It was necessary to dilute the samples with a large amount of methane (> 97 mole %) to achieve satisfactory counting characteristics.⁽¹³⁾ Counting efficiency was checked from time to time against a standard external Co^{60} source; no corrections were ordinarily necessary, except for SF_6 samples, which had to be counted at concentrations of much less than 1% (these count rates were at very low efficiency, 20% or less). Solid samples obtained from the chemical separations described below were converted to SO_2 to be counted after ignition with phosphorus as described by Merritt and Hawkings.⁽¹³⁾ A few solid samples, including

most of the mercaptan precipitates, were counted on an end-window beta counter which was standardized against the internal counter. Absorption corrections were based on tables prepared by Herber. (14)

Chemical separations

The sample tubes were broken open with a magnetic plunger in a vacuum line, and the activity was recovered in two fractions, the gaseous activity, and that which remained on the walls of the tube after the gas was pumped out. Ordinarily the gross gaseous activity was first determined, then the gaseous fraction was absorbed into an alkaline solution for analysis. The activity from the walls was removed by washing the broken fragments with a similar alkaline solution. Tests showed that this method was effective in removing the activity from the walls. These solutions contained known amounts of carriers for the compounds of interest. (In some cases the carrier was added as a gas; for example, H_2S was added to irradiated CH_3SH samples when the tube was broken.) In general, sufficient carrier was added to give 5 to 50 mg of precipitate.

Most of the separation involved only $S^{=}$, $SO_3^{=}$, and $SO_4^{=}$. It is known that at room temperature the exchange rate in solution is negligible for these species. (15) Elemental sulfur in trace amounts will exchange with and appear as $S^{=}$; this fact was used in analysis, so that S and $S^{=}$ were determined together in the washings from the walls (if any form of $S^{=}$ were present). (15) Any SO_3 formed was recovered as $SO_4^{=}$ in the washings from the walls. The only material determined, other than $S^{=}$, $SO_3^{=}$, or $SO_4^{=}$, was the total mercaptan fraction, as described below. Care was taken to remove oxygen from the reagents when $SO_3^{=}$ was to be determined, and the separation was carried out under a nitrogen atmosphere.

Where $S^{=}$, $SO_3^{=}$, and $SO_4^{=}$ were all to be determined in the same sample, sample and carriers in alkaline solution were placed in a glass vessel which was part of a gas train. A solution of $CuCl_2$ was added to precipitate CuS . The solution was then acidified with HCl , and argon gas was bubbled through the solution to carry the SO_2 evolved into an absorbing vessel containing alkaline H_2O_2 , where it was absorbed and oxidized to $SO_4^{=}$. The CuS was then filtered out of the first solution, and $SO_4^{=}$ was precipitated as $BaSO_4$. In many cases, it was necessary to analyze for only two of the components; the process was simplified accordingly.

Mercaptans were determined by use of CH_3SH as a carrier if necessary, by exposing the gaseous sample to a saturated $HgCl_2$ solution, in which the precipitate $Hg(CH_3S)Cl$ is formed.⁽¹⁶⁾ The H_2S was first removed by exposing the sample to a $CuCl_2$ solution. It appears likely that trace amounts of other mercaptan activities would coprecipitate with the methyl mercaptan salt.

RESULTS

Errors

The two basic sources of error in the data are (a) error in measuring the sizes of the samples and the aliquots taken for counting, and (b) the statistical counting error.

In general, the total size of the sample was known from pressure and volume measurements to $\pm 1\%$. In the very smallest samples this increased to $\pm 5\%$, but this was compensated to some extent, because it was not necessary to take aliquots for counting. Aliquots were measured manometrically in a calibrated volume; the error here was generally $\pm 2\%$, except in the very small SF₆ samples where it was in the range of ± 5 to 10% . The error in carrier standardization and delivery was about $\pm 2\%$.

Whenever possible, the samples were counted for a length of time sufficient to hold the statistical counting error to $\pm 1\%$. The background of the counting tube, which was frequently checked, was in the range of 60 to 150 counts per min during the course of these experiments. Portions of the sample that gave counting rates of this order could not be so accurately determined, and in some cases the error approached $\pm 10\%$. This was not an important problem, since it was not generally necessary to determine the activity in these relatively inactive fractions to a high degree of accuracy.

When the solid precipitates were counted (all mercaptan samples and certain others), an error in reproducibility was found which was in the range of $\pm 10\%$ and which was probably due to inhomogeneities in sample thicknesses.

From summation of the individual errors the cumulative estimated error is seen to be $\pm 4\%$ in most cases; in the special cases mentioned it may be higher. Most data are reproducible within this range. Variations in excess of this, such as were obtained in the results from irradiation of SO₂, are believed due to variations in the condition of the walls of the capsule, or possibly due to reactions of trace impurities.

Experimental data

Tables I through V show the distribution of S^{35} activity by chemical form as recovered from the various gases studied. The percentages reported in the columns are percentages of the total activity actually recovered for the given sample, except as noted in Table V. The data in the column headed Gaseous fraction, total, are obtained from a direct gross count of the gaseous products, and not from addition of the separate gaseous compounds. The data in the column headed Wall fraction, total, were obtained either from addition of the separately analyzed fractions of activity from the wall, or from oxidation to $SO_4^{=}$ of all activity recovered from the wall. In many cases a complete accounting of the activity was not made for every sample, and thus a particular number may be based on fewer samples than indicated in the given set.

The errors given are probable errors, obtained from the deviations of the actual data from the mean.

Samples noted by Quartz wool in the Additive column of Tables I and II were irradiated in tubes packed with quartz wool (previously described in the Experimental section).

DISCUSSION

The breakup process

To explain the reaction of the S^{35} produced by $S^{34}(n,\gamma)$ reaction, it is first necessary to consider the process of breakup in the original molecule. Each of the gamma rays following neutron capture causes the nucleus to recoil with an energy

$$E = E_{\gamma}^2 / 2Mc^2,$$

where E_{γ} is the energy of the gamma ray, M is the mass of the atom concerned, and c is the velocity of light. In $S^{34}(n,\gamma)S^{35}$, where the total energy of the gamma rays is 6.98 MeV, ⁽¹⁷⁾ the maximum possible recoil energy is 760 eV, and the average recoil energy would be considerably less. The exact recoil energy depends on the energies and angular correlations of the gamma rays involved. These have not been determined for $S^{34}(n,\gamma)$ because of the radiations from $S^{32}(n,\gamma)$ present in much greater quantity in the natural sulfur targets employed. ⁽¹⁸⁾

These recoil energies of hundreds of electron volts may be compared with the energies of bonds between sulfur and other elements: H-S, 3.8 eV; ⁽¹⁹⁾ S-O (in SO_2), 5.3 eV; ⁽²⁰⁾ C-S, 2.4 eV; ⁽¹⁹⁾ and S-F (in SF_6), 3.7 eV. ⁽²⁰⁾

Thus the energy required to break the bonds is much less than that available from the recoil process.

The breakup of a molecule subsequent to such an impulse given to one of its atoms was first studied by Suess ⁽²¹⁾ and has more recently been investigated by Hsiung and Gordus. ⁽⁷⁾ These authors have developed the theory of breakup in detail for the case in which an atom is connected to the rest of the molecule by a single bond. Their results show that the ratio of the recoil energy required to break the bond to the dissociation energy of the

bond depends on the relative masses of the atoms involved. Unless the atom given the impulse is bonded to a very light atom such as hydrogen, this ratio is not more than about two or three. For an S-H bond it is roughly 35.

The effect of multiple bonding on these considerations is not known. If, in a complicated molecule such as SF₆, a large amount of kinetic energy is carried away by some of the fluorine atoms in dissociating, it is possible that one or more atoms might remain bound. It is difficult to estimate the probability that this will happen.

The kinetic energy of the recoiling S³⁵ atom will, in any event, be much less than that required for it to be ionized due to its own velocity in the gas. (22) If the gamma transitions are internally converted, ionization is to be expected. (23) While the exact decay scheme is not known for S³⁴(n,γ)S³⁵, the net spin change is relatively small (1/2 → 3/2) so that the ground state will probably be reached by radiations of low multipolarity that have low conversion coefficients. Further support for this hypothesis comes from the fact that the known gamma rays resulting from the S³²(n,γ)S³³ reaction are primarily of high energy and low multipolarity. The known nuclear-energy levels in S³⁵ are very similar to those found in the S³³ nucleus. (24) One would therefore expect the radiations following neutron capture to be similar. From these considerations the probability of forming S³⁵ in an ionized form is believed to be small.

Therefore, it would appear that the original molecule is likely to break up into atoms or radicals, with the possible exception of H₂S, which would have the largest mass-dependent factor hindering dissociation. The results shown in Table I indicate that this molecule does break up; when O₂-H₂S mixtures were irradiated, only 3% of the activity was recovered as H₂S. Other molecules would be expected to break up if H₂S does, and the

results in the other tables substantiate this. Whether the S^{35} is always left as atomic sulfur after the breakup is an uncertain point, which is further discussed when we consider the results obtained from irradiating mixtures of various gases with NO.

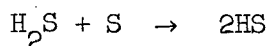
Reactions in H_2S
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As shown in Table I, more than 80% of the  $S^{35}$  from irradiated  $H_2S$  appears in the gas phase and follows the chemistry of  $H_2S$ . This yield increases slightly with increasing pressure, but is not greatly affected by the addition of argon or by packing the tubes with quartz wool. (The activity observed may not be entirely  $H_2S$ , but may include  $H_2S_2$  which would follow the  $H_2S$  chemistry.)

The fact that argon has no noticeable effect on yields of  $S^{35}$  activity indicates that hot reactions are not responsible for incorporating the activity into its final form. This point will be discussed later.

The reactions responsible for producing the  $H_2S$  activity very likely take place in the gas phase rather than on the walls, as very little activity is found deposited on the walls. The amount of material which is recovered on the walls appears to decrease with increasing  $H_2S$  pressure, but addition of quartz wool does not noticeably affect the results. This behavior is reasonable if the reaction which incorporates the activity into the gas phase is pressure dependent, thereby competing with slower reactions that lead to the material found on the walls.

The nature of such a reaction can be inferred, if it is assumed that the  $S^{35}$  is left as a bare atom following breakup, as is most likely. The abstraction reaction



is endothermic and will not take place with thermal S atoms. It is therefore

likely that the  $S^{35}$  adds to  $H_2S$  to form a  $H_2S-S$  complex, which then undergoes further reaction or rearrangement to form  $H_2S^{35}$  or  $HS^{35}SH$ . The slower reactions leading to deposits on the walls may involve, for example, reactions with impurities and radiation products.

Note that the irradiation of  $H_2S-O_2$  mixtures results chiefly in the production of  $S^{35}O_2$ . This was also the principal product from the irradiations of mixtures of  $O_2$  with  $SO_2$  and  $SF_6$ . Thus, if  $O_2$  is present, it appears that the reaction to produce  $SO_2$  occurs regardless of the original chemical form of the  $S^{35}$ . The few per cent of  $S^{35}O_2$  recovered from irradiation of  $H_2S$  without added  $O_2$  must be caused by trace amounts of  $O_2$  or by reactions at the walls.

#### Reactions in $SO_2$

It can be seen from Table II that the data obtained from irradiations of  $SO_2$  are complicated and tend to scatter considerably. The activity was found in four fractions: gaseous  $SO_2$  (no other gaseous activity was found), and fractions from the walls which followed the chemistry of  $S^=$ ,  $SO_3^=$ , and  $SO_4^=$ , respectively. The  $S^=$  fraction presumably represents sulfur, and the  $SO_4^=$  fraction any  $SO_3$  which is formed; the exact nature of the  $SO_3^=$  fraction is unknown. There appeared to be some correlation between the  $SO_2$  and  $SO_3^=$  fractions; in individual samples in which the yield of one of the fractions was significantly lower than average, the yield of the other was generally higher than average, and vice versa.

The following may be noted from Table II. (1) The yield of gaseous  $SO_2$  increases with increasing pressure. (2) Argon has little effect on the yields; this indicates that the reactions involved are those of thermal species, as will be discussed later.

The increase in  $\text{SO}_2$  yield with pressure would appear to indicate that a gas-phase reaction is involved in producing  $\text{SO}_2$  activity; however, there are also indications that the walls are strongly involved in determining the chemical form of the activity. These indications include the apparent correlation between  $\text{SO}_2$  and  $\text{SO}_3$  described above, the quartz-wool effect, and mechanistic considerations which will be described.

The nature of the gas-phase reaction that produces  $\text{S}^{35}\text{O}_2$  is not clear. If the  $\text{S}^{35}$  is left as atomic sulfur by the recoil process, the thermal  $\text{S}^{35}$  atoms cannot react with  $\text{SO}_2$  to abstract oxygen, as this would be highly endothermic. A reaction of  $\text{S}^{35}$  and  $\text{SO}_2$  might, however, involve an addition process, such as postulated for the  $\text{H}_2\text{S}$  system, whereby a  $\text{S}^{35}\text{—SO}_2$  complex is formed that yields  $\text{S}^{35}\text{O}_2$  by subsequent reaction.

The importance of wall reactions is indicated by the implications of the large amount of  $\text{S}^{35}$  recovered there. The  $\text{S}^{35}\text{O}_3$  fraction is very likely formed there, particularly in view of the apparent correlation between this fraction and  $\text{S}^{35}\text{O}_2$  mentioned earlier. The  $\text{SO}_2$  activity can result from a precursor adsorbed on the walls, but once  $\text{S}^{35}\text{O}_2$  is formed, it will become indistinguishable from the large amount of inactive  $\text{SO}_2$  present. It is also very difficult to devise a path for the production of  $\text{SO}_3$  (recovered as  $\text{SO}_4$ ) other than by reaction at the wall; gaseous  $\text{SO}_2$  cannot be an intermediate, as it is mainly inactive, and oxidation of  $\text{S}^{35}$  atoms or of  $\text{S}^{35}\text{O}$  fragments by trace oxygen, if this were present, would tend to produce  $\text{S}^{35}\text{O}_2$ . This tendency is supported by the results in the samples to which  $\text{O}_2$  was added: with increasing  $\text{O}_2$  pressure, the yield of  $\text{S}^{35}\text{O}_2$  increases at the expense of the activity from the walls. The  $\text{SO}_2$  is also the predominant product from the irradiation of mixture of other gases with  $\text{O}_2$ , as will be seen.

The fact that quartz wool has little effect on the reaction at a pressure of approximately 10 cm of Hg, though wall reactions appear to be important, implies that wall reactions must be the predominant reactions at this pressure. Thus, even a major part of the  $\text{SO}_2$  fraction must come from wall reactions at this pressure, as was also implied in the  $\text{SO}_2$ - $\text{SO}_3$  correlation. The scatter in the data can be readily explained when one considers how important the exact nature of the walls and the impurities adsorbed on them must therefore be in determining the chemical fate of the  $\text{S}^{35}$ . (Not more than  $10^{10}$  atoms of  $\text{S}^{35}$  were produced in any one sample; a monolayer of gas on the walls would amount to roughly  $10^{15}$  to  $10^{16}$  molecules.) At higher pressures the gas-phase reaction that gives  $\text{S}^{35}\text{O}_2$  appears to become more important, as would be indicated by the suggestion of a difference between samples in tubes containing quartz wool and those in plain tubes. The considerable scatter in data makes interpretation difficult.

In irradiations of  $\text{SO}_2$ - $\text{H}_2$  mixtures the  $\text{S}^-$  fraction is greatly increased relative to the corresponding fraction from  $\text{SO}_2$  alone, but only 4% of  $\text{H}_2\text{S}$  is formed. The reason for the increase of  $\text{S}^-$  may be that the  $\text{H}_2$  reacts with the oxidizing species on the walls, which are responsible for producing the  $\text{SO}_3^-$ ,  $\text{SO}_4^-$ , and perhaps part of the  $\text{SO}_2$  fractions. The  $\text{S}^{35}$  can therefore collect on the walls as sulfur, which follows the  $\text{S}^-$  chemistry.

#### Epithermal reactions

Tests for reactions proceeding by hot or epithermal mechanisms were made in  $\text{SO}_2$  and in  $\text{H}_2\text{S}$  by adding argon as an inert moderator to the sample irradiated (see Tables I and II). Such reactions, which involve reactions of recoil atoms with a few electron volts or tens of electron volts of energy, were first described and characterized in reactions of recoil tritium with

methane by Estrup and Wolfgang.<sup>(6)</sup> In the experiments with argon and  $S^{35}$  in our work, no significant deviation from the yields of activity obtained in the absence of argon was observed, although the mole fraction of argon was typically in the range of 80 to 90%.

According to the theory developed by Estrup and Wolfgang, the sensitivity of these reactions to the effect of the moderator is governed by (a) the mass ratio of the inert gas to the recoil, (b) the cross section for the hot reaction, and (c) the range of energy in which the reaction is possible. The  $Ar^{40}$  is a better moderator for  $S^{35}$  than  $He^4$  is for T, and it seems unlikely, from mechanistic considerations, that any reaction involving a hot  $S^{35}$  would proceed with greater efficiency or over a wider range of energy than the tritium-methane reaction, so that such reactions of  $S^{35}$  should be at least as sensitive to moderation as that of tritium with methane. However, in the latter reaction, as well as in others of this type which have been reported,<sup>(3)</sup> the addition of approx 85% moderator was sufficient to reduce the yield of hot products to approx 30% or less of that obtained in unmoderated systems. For this reason it is felt that the reactions of  $S^{35}$  in  $SO_2$  and  $H_2S$ , which lead to the final products observed, are those of thermal species.

Reactions in  $SF_6$   
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As shown in Table III, the S^{35} activity produced by irradiating SF_6 is recovered principally (approx 80%) as deposits on the walls of the tube. These deposits follow the chemistry of S^- or $[SO_3^- + SO_4^-]$. The remainder is found in a form which is carried by SO_2 and may be SO_2 , or perhaps SF_4 . No activity was recovered which did not hydrolyze to SO_3^- ; this places an upper limit on the production of $S^{35}F_6$ of about 5%. The exact limit is uncertain because of the considerable difficulty in counting SF_6 samples.

The SF_6 is very inert; it is likely that the S^{35} simply diffuses to the walls and reacts there to give the products which are recovered. Note that the products found on the walls in this case are similar to those found on the walls in irradiated SO_2 ; this would indicate that the conditions at the walls, rather than the original form of the molecule, appear to determine the oxidation state of this deposited activity.

After the addition of oxygen, the chief product (47%) is SO_2 ; some of the gaseous activity was not recovered, and may have consisted of oxyfluorides. About 28% of the activity was recovered in the $[SO_3^- + SO_4^{2-}]$ fraction from the walls. This is of particular interest as SO_2 is the principal product even though the sulfur was originally in the +6 state. Here the environment rather than the original oxidation state determines the final oxidation state.

Reactions in methyl mercaptan and thiophene

One can explain the high recovery of the activity in the form of H_2S from irradiations of CH_3SH (Table IV) by postulating reactions similar to those proposed for the H_2S system. Thus, for example, an S^{35} atom may attack the SH group in CH_3SH , resulting in an eventual rearrangement to give H_2S^{35} . Other types of reaction can lead to the production of H_2S^{35} ; these include hot reactions, or reactions with radiation-produced materials, such as are postulated to explain the production of H_2S from thiophene below.

The reactions in CH_3SH appear to be rather complex; a few percent of mercaptans was produced, as well as a fairly large fraction of gas-phase activity that did not give any hydrolysis product that was recovered in the analysis of the gaseous material. This fraction presumably includes such materials as thioethers, etc.

The H_2S^{35} is an important product of the irradiation of thiophene, where the only mechanisms available for its production are hot hydrogen abstractions and/or reactions with radiation products. A large part of the activity appears not to undergo such reaction, but instead diffuses to the wall and is found in S^- or $[\text{SO}_3^- + \text{SO}_4^-]$ from the walls, or as gaseous SO_2 .

As shown in Table IV, the addition of oxygen to these two systems results in the production of SO_2 plus wall oxides to the extent of only about 50 to 70%, compared with approx 90% in other systems studied. It would seem that these systems, and the reactions which take place in them, are quite complex. More efficient analytical techniques, such as gas chromatographic methods, will be needed to resolve these complexities.

Effect of the addition of NO

The irradiation of mixtures of several gases with NO led to results which were strikingly different from those obtained with NO absent. The NO, which has an unpaired electron, is often used as a radical scavenger. It is known to inhibit reactions of free radicals, apparently by reacting with the radicals to form addition compounds which are relatively inert.

The results of these irradiations are shown in Table V, and may be summarized as follows:

In H_2S -NO mixtures the activity was recovered primarily in the gaseous phase and hydrolyzed almost completely to S^- . However, this material could be distinguished from H_2S by its high reactivity toward the walls of the vacuum line and toward the counting tube in particular.

In SO_2 +NO and SF_6 +NO mixtures the activity was also recovered primarily in the gaseous phase; about 75% of this gaseous activity followed the chemistry of SO_3^- and SO_4^- (which were determined together) after hydrolysis. The

remainder followed the $S^{\bar{}}$ fraction. These results contrast with those from irradiations made without NO, where large amounts of the activity appeared on the walls, and no hydrolysis of gaseous activity to $S^{\bar{}}$ was found.

It is clear that in all these cases the NO reacts with the S^{35} and produces compounds which are not formed in the absence of NO. The difference in hydrolysis products observed, i.e., $[SO_3^{\bar{}} + SO_4^{\bar{}}]$ compared with $S^{\bar{}}$, indicates that more than one such compound is formed, depending on the sulfur-containing gas used. The dependence on the gas used may be the result of one or both of the following effects: (1) The parent gas, as well as the S^{35} primary fragment and the NO, participates in the reaction that determines the final chemical form of the S^{35} . It is difficult to explain the results from the SF_6 irradiations in this way, however, due to the inert character of SF_6 . (2) The chemical form of the S^{35} following breakup may depend on the original chemical form of the molecule. This would mean either that the molecule is not completely broken apart by the gamma-ray impulse in a significant number of cases, or, if it is, that the sulfur atom produced from different molecules can be left in different electronic states. While incomplete molecular breakup seems improbable, it has not been eliminated, particularly in such a complex case as SF_6 . There is a possibility that different electronic states of atomic sulfur are formed which react to give different products. This is supported by the observation that atomic oxygen, produced in different electronic states by photolysis, has been found to undergo different reactions with organic molecules depending on the electronic state produced. (25,26) It is hoped that further studies will resolve these possibilities.

SUMMARY

Breakup of the original molecule has been shown to be general following the $S^{34}(n,\gamma)S^{35}$ reaction but there remains a possibility that not all bonds will be broken, depending on the nature of the original species.

Except possibly for the results obtained with added NO, oxidation or reduction of the sulfur activity appears to depend upon the surroundings-- walls, reactive gases, etc., rather than upon the oxidation state or nature of the original molecule.

The H_2S^{35} has been found to be a major product in irradiations of H_2S , CH_3SH , and thiophene. (The H_2S^{35} fraction may also include H_2SS^{35} .) The results of SO_2 irradiations are complex; an important contribution to the reactions appears to involve the walls. Oxidation on the walls seems to take place readily when gas-phase reactions do not compete; this is not unexpected in view of the ease with which oxidation occurs in C^{11} recoils (4) and in S^{35} formed in crystals. (9)

Implicative results were obtained from irradiations of various gases mixed with NO. Although S^{35} was recovered in gaseous compounds that were not definitely identified, the study of the hydrolysis products of these compounds implies that the chemical form of the S^{35} immediately following breakup may vary with the chemical form of the original compound.

No epithermal reactions have been identified as such for S^{35} recoils; they have probably been ruled out in the SO_2 and H_2S systems. The results from the irradiation of CH_3SH or thiophene suggest that hot reactions may take place in these systems.

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Table I. Chemical form of S³⁵ recovered from irradiated H₂S.

P H ₂ S (cm Hg)	Additive	P Additive (cm Hg)	Gaseous fraction*			Wall fraction			Number of samples
			H ₂ S	SO ₂	Total	S,S ⁼	SO ₄ ⁼	Total	
1.7	---	---	---	11	81	4	15	19	1
10	---	---	85	5±4	89±4	4±1	7±3	11±5	4
25	---	---	---	---	95±1	2	2	5±1	2
47	---	---	---	10±5	97±1	1	2	3±1	2
10	Quartz wool	---	---	3	97	1	2	3	1
49	Quartz wool	---	93	5±5	99±1	---	---	1±1	2
6	Ar	49	---	---	93	---	---	7	1
10	Ar	57	85	7	92±5	3±2	5±4	8±5	2
10	O ₂	1.6	3	≥ 40	74±3	11	15	26±3	2
10	O ₂	10	3	≥ 70	79±1	5±1	16±2	21±2	2

* Once it was determined that the bulk of the gaseous activity consisted of H₂S, usually only the total gas count and the SO₂ portion were determined.

Table II. Chemical form of S^{35} activity recovered from irradiated SO_2 .

P_{SO_2} (cm Hg)	Additive	P_{Additive} (cm Hg)	Gaseous fraction SO_2	Wall fraction			Total	Number of samples
				$S, S^=$	$SO_3^=$	$SO_4^=$		
1	---	---	20±5	21±7	22±2	37±4	80±5	3
8 to 10	---	---	39±4	20±4	12±2	31±6	61±4	6
55 to 68	---	---	75±13	7±2	15±10	11±4	25±13	3
8 to 10	Quartz wool	---	47±10	20±4	7±2	24±9	53±10	3
70	Quartz wool	---	64±6	15±3	6±1	16±4	36±6	2
8	Ar	60	54±9	14±3	11±3	21±5	46±9	3
10	O_2	1.3	58±3	5±3	1±1	36±1	42±3	2
10	O_2	10	56±3	1	1	42	44±3	2
10	O_2 , Quartz wool	10	61±2	2	1	36	39±2	2
10	O_2	60	79±4	5±3	4±2	11±3	21±4	2
10	H_2	10	21±6*	55±1	19±3 [†]		74±4	2

* H_2S , 4±1%.

†, $SO_3^=$ plus $SO_4^=$.

Table III. Chemical form of S³⁵ activity recovered from irradiated SF₆.

P _{SF₆} (cm Hg)	Additive	P _{Additive} (cm Hg)	Gaseous fraction		Wall fraction			Number of samples
			SO ₂	Total	S,S ⁼	[SO ₃ ⁼ + SO ₄ ⁼]	Total	
5	---	---	23	18*	46	31	77	1
11	---	---	9±1	19 [†]	31±7	51±3	81±10	2
5	O ₂	5	47±2	69±2 [†]	2±1	28±1	31±2	2

* SO₂ used as basis for total. In all gas counts of SF₆ the counting accuracy was poor, approaching ±40% in some cases.

[†] Gas count used as basis for determining total.

Table IV. Chemical form of S³⁵ activity recovered from irradiated CH₃SH and Thiophene.

Gas	P _{Gas} (cm Hg)	Additive	P _{Additive} (cm Hg)	Gaseous fraction				Wall fraction			Number of samples
				SO ₂	H ₂ S	Mercaptans	Total	S,S ⁼	[SO ₃ ⁼ + SO ₄ ⁼]	Total	
CH ₃ SH	17 to 24	---	---	5±3	44±8	5±2	96±1	2	1	4±1	4
CH ₃ SH	18	O ₂	12	52±6	39	---	86±2	7±2	7±2	14±2	2
Thiophene	6 to 7	---	---	17	29±5	8±4	63±2	21±1	16±1	37±2	3
Thiophene	6	O ₂	7	41	---	2	73	14	12	26	1

Table V. Chemical form of S^{35} recovered from irradiations of mixtures of various gases with NO.

Gas	P _{Gas} (cm Hg)	P _{NO} (cm Hg)	Gas fraction			Wall fraction			Number of samples
			[SO ₃ ⁼ + SO ₄ ⁼]	(S ⁼)	Total	S,S ⁼	[SO ₃ ⁼ + SO ₄ ⁼]	Total	
H ₂ S	7	2	1	> 40	82	8	9	17	1
H ₂ S	8	8	1	> 40	*	5	5	10±1	2
SO ₂	19	1	---	---	88	3	8	12	1
SO ₂	10	10	74±2	17±4	†	5±2	5±2	10±4	2
SO ₂	20	10	---	---	95±1	1±1	4±2	5±1	2
SF ₆	11	3	---	---	88±4	3±1	9±5	12±4	2
SF ₆	12	10	71±5	21±4	†	4±2	4±1	8±1	2

* Not determined. Total activity calculated from Au¹⁹⁷(n,γ)Au¹⁹⁸ monitor; believed accurate to ± 15%.

† Sample dissolved directly without taking gross gas count.

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