[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Reactions of Elemental Sulfur. III.[1] A Preliminary Study of the Conversion of Hexatomic to Octatomic Sulfur

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Hexatomic sulfur, S_6, is stable in organic solvents for long periods at 65° and below but is converted into normal octatomic sulfur in the presence of triethylamine. The rate is critically dependent upon minute amounts of impurities in the sulfur; it has been shown that sulfur dioxide in the presence of amine is a powerful cocatalyst. The $S_6 \rightarrow S_8$ conversion proceeds by way of a polymerization and depolymerization. The high polymer has been detected and the changes in its concentration observed by both light absorption and light scattering, and a similarity noted, as to the rate and kinetic type of its depolymerization, with the product of strong irradiation of ordinary sulfur in organic solvents. Certain points of the mechanism are discussed. The work is being continued.

Introduction

The molecular form of sulfur consisting of an 8-membered ring is thermodynamically stable with respect to all other known forms of sulfur at room temperature. Hexatomic sulfur, S_6,[2,3] the next best characterized molecular form of sulfur, is stable for long periods of time in the crystalline state but is rapidly converted into S_8 in solution in the presence of amines and certain other catalysts. Since the reaction $4S_6 \rightarrow 3S_8$ presents an obvious problem of mechanism, we have undertaken a survey of its conditions in the hope of discovering what intermediates are involved.

Experimental Approach

Hexatomic sulfur has been prepared by Engel[2] and by Aten[3] and has been prepared and characterized in this Laboratory by Whitfield[4] and Meguerian.[5] Its molecular weight is clearly shown by cryoscopic studies. Frondel and Whitfield[6] have determined the dimensions of the unit cell by X-ray methods, finding that the unit cell contains 18 sulfur atoms, consistent with the hexatomic formula. Figure 1 shows the absorption spectrum of S_8, the usual crystalline form of sulfur, together with that of S_6 and of the sulfur produced by long irradiation of a benzene solution of sulfur.[5] The latter species we have designated as S* to suggest photoactivation but it is not an electronically excited species, being stable like S_6 in solution under non-catalytic conditions. The extinction coefficients in Fig. 1 have been calculated using gram-atomic weights per liter as the unit of concentration so that a vertical line at any point intersects the three curves at points indicating the relative light absorptions of equal masses of sulfur in the three forms. The irradiation of sulfur solutions produces a steadily increasing light absorption from wave lengths of 303 mμ up (Fig. 2), but it is not certain that the spectrum of the most intensely absorbing of these solutions corresponds to a total absence of S_8.

The spectral properties of S_8, S_6 and S* afford the possibility of following interconversions among them by observations at suitably chosen wave lengths. For example, at the isosbestic point of S_8 and S_6 near 350 mμ, the presence of S* will show itself by a more than doubling of the optical density. At the isosbestic point of S_8 and S*, near 300 mμ, it is possible to distinguish S_6 from either of these species. In addition to the spectroscopic method, we have available[5] a titrimetric method with standard solutions of triphenylphosphine which distinguishes the rapidly reacting S_6 and S* from the slowly reacting S_8. This titration method was the basis of the first set of rate measurements on the conversion of S_6 to S_8.

Table I shows 12 experiments designed to discover the effectiveness of various conditions and catalysts for converting S_6 to S_8, the course of the reaction being followed in each case by the triphenylphosphine titration of aliquot samples. At 25° in toluene a solution of hexatomic sulfur remained unchanged for days and this result was unaffected by the inclusion of 1% of methanol or of acetic acid in the toluene. Likewise, there was no observable thermal transformation of S_6 to S_8 in *m*-xylene at 65.6° over a period of days. In mesitylene at 106° S_8 appeared at a measurable rate, the conversion being half complete in 700 minutes. Thus, there is either a slow thermal mechanism for this reaction or it is sensitive to amounts of adventitious catalysts smaller than we could control in this type of experiment.

At 65.6° a 0.00324 *M* solution of benzoyl peroxide in *m*-xylene caused a 0.085 gram-atomic solution of S_6 to be 40% converted into S_8 in 7800 minutes.

In three experiments in toluene at room temperature a few milligrams of untreated alumina proved to be a powerful catalyst for the conversion of S_6 to S_8. Amounts of different samples of the order of 10 mg. of alumina in 20 cc. accomplished half-conversion in times varying from 2.5 to 57 minutes. Boiling with dilute hydrochloric acid rendered the alumina inert. Another solid substance which, while insoluble in benzene, appeared to promote the S_6 to S_8 reaction rapidly was sodium carbonate, which accomplished half-conversion in 28 minutes in a single experiment. Table I leaves the general impression that the conversion of S_6 to S_8 is promoted by free radicals, by temperatures as high as 100° and by basic substances but not by acids. The final experiment shown in Table I indicates that the amphoteric substance, α-hydroxypyridine, is not a catalyst for this conversion.

The Problem of Reproducibility.—Since bases are known to bring about the conversion of metastable forms of sulfur to S_8 as well as the redistribution of sulfur between the elementary state and polysulfide chains, we chose triethylamine as a standard catalyst for the further investigation of this reaction. A number of experiments were carried out on solutions of S_6 in benzene containing from 0.01 to 0.11 gram-atomic weights per liter, most of the experiments being conducted upon the more concentrated sulfur solutions. Triethylamine was used at concentrations varying from 0.0004 to 0.05 *M*. The benzene used was thiophene-free; the triethylamine was carefully redistilled and material boiling over a narrow range was used. The hexatomic sulfur was subjected to a variety of treatments for purification. In a few instances it was used as it crystallized from the first chloroform or carbon tetrachloride extract. In most cases it received numerous recrystallizations in the presence or absence of reagents, such as sulfur monochloride or iodine, designed to remove traces of impurities. In experiments having no known differences in experimental conditions, the measured rate of conversion of S_6 to S_8 varied by factors as great as 3,000. No procedure was found during the course of this work which permitted duplication of the experimental results from one experiment to another, but it soon became apparent that the crude S_6 from the acidification of thiosulfate contained powerfully catalytic impurities which could be greatly reduced in amount by a series of recrystallizations, one of which would be carried out in the presence of a small amount of sulfur monochloride. For the purpose of drawing what conclusions these data permit, the results of 72 runs are presented statistically in Table II. The time

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[1] Part II: P. D. Bartlett and R. E. Davis, THIS JOURNAL, **80**, 2513 (1958).

[2] M. Engel, *Compt. rend.*, **112**, 866 (1891).

[3] A. H. W. Aten, *Z. physik. Chem.*, **88**, 321 (1914).

[4] R. E. Whitfield, Thesis, Harvard University, 1949.

[5] P. D. Bartlett and G. Meguerian, THIS JOURNAL, **78**, 3710 (1956).

[6] C. Frondel and R. E. Whitfield, *Acta Cryst.*, **3**, 242 (1950).

TABLE I

EFFECT OF CONDITIONS ON STABILITY OF S_6 IN SOLUTION

Run no.	Temp., °C.	Solvent	Substance added	$(S_6)_0$, g.-at./l.	Min.	% Conversion to S_8
1	25	Toluene	CH_3OH, 1%	0.092	8,700	None
2	25	Toluene	CH_3COOH, 1%	.091	8,550	None
30	65.6	*m*-Xylene	None	.086	13,140	None
31	65.6	*m*-Xylene	None	.095	7,500	None
11	106	Mesitylene	None	.096	700	50
32	65.6	Mesitylene	Benzoyl peroxide 0.00324 *M*	.085	7,800	40
33	65.6	*m*-Xylene	Benzoyl peroxide 0.00862 *M*	.084	6,000	50
58	23.8	Toluene	Al_2O_3, 10 mg. in 20 cc.	.096	57	50
63	22.9	Toluene	Al_2O_3	.102	24	50
64	23.4	Toluene	Al_2O_3	.090	2.45	50
67	24.6	Benzene	Na_2CO_3, solid	.094	28	50
B15	24.9	Benzene	α-Hydroxypyridine 0.0109 *M*	.0543	4,200	None

TABLE II

CONVERSION OF S_6 TO S_8 WITH TRIETHYLAMINE—DISTRIBUTION OF HALF-CONVERSION TIMES IN 72 RUNS AT 25°

Time of half-conversion, min.	No. of runs
0.3–5	8
5–10	16
10–15	7
15–20	4
20–25	8
25–50	15
50–100	8
100–200	0
200–300	2
300–400	0
400–500	1
500–1000	1
>1000	2

of half conversion to S_8 is arbitrarily chosen as a crude measure of the speed of the reaction, but it has no kinetic significance, since the reaction corresponded to no simple order and indeed, as will appear below, the reaction consisted of two successive steps which responded differently to changes in experimental conditions.

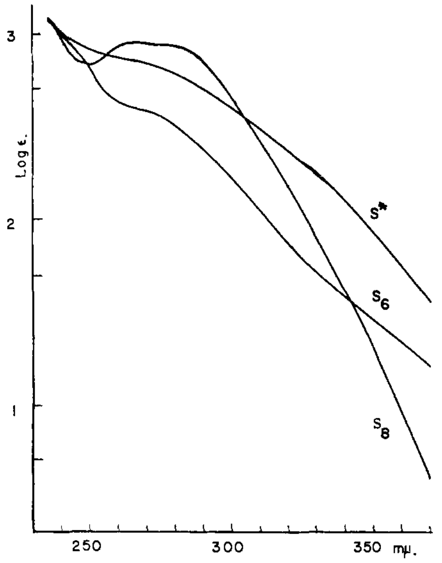

Fig. 1.—Spectra of S_8, S_6 and irradiated sulfur.

Although the time of half-conversion varied from 0.3 to over 1,000 minutes, only 6 runs out of 72 showed half-times greater than 100 minutes. There appears to be no correlation between the rate of reaction and the concentration of triethylamine nor of S_6, since the runs containing the smallest concentrations of each of these reagents in turn appear to be reasonably uniformly distributed over the range of rates characterizing the entire series of experiments. In five experiments the solution of hexatomic sulfur was aged for lengths of time from days to weeks before the experiment and these experiments also showed a random distribution as to speed. Only three conditions showed a clear correlation with the rate of reaction. Three runs in which sulfur dioxide was introduced in concentrations of the order of 10^{-6} *M* in addition to triethylamine all showed periods of half conversion of less than ten minutes. Two experiments on raw, unrecrystallized S_6 gave half-times of 0.3 and 2.2 minutes, while, by the addition of small concentrations of iodine, the rate of conversion of this same raw S_6 was retarded to give half times of about 800 and 1,000 minutes. The quest for reproducibility in these rate runs has been continued in subsequent work in this Laboratory, which will be the subject of a further publication.

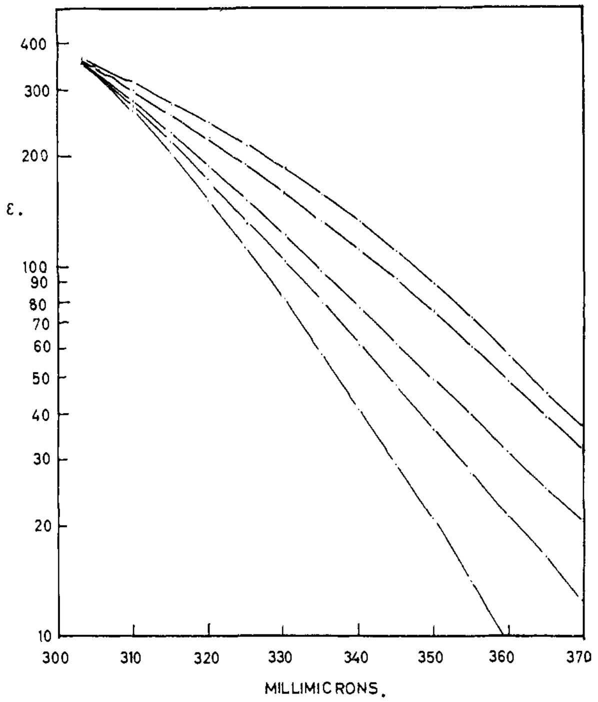

Fig. 2.—Portion of spectrum of a solution of ordinary sulfur in benzene, irradiated with a sun lamp for different periods.

Spectroscopic Studies: the Two-stage Nature of the Conversion of S_6 to S_8.—It is apparent on general kinetic grounds that the conversion of $4S_6$ to $3S_8$ must proceed by way of some kind of intermediate since any one-step way of accomplishing such a result would be mechanically highly improbable. In any such situation where it is desired to detect the presence of an intermediate, it is convenient if the starting material and product have an isosbestic point where their optical absorptions are identical. In the present case, if S_6 were to change into S_8 without passing through a third substance as intermediate, the optical density at the isosbestic point indicated in Fig. 1 should remain unchanged throughout the reaction.

A series of runs was carried out in which the optical density at wave lengths near 345 mμ was recorded as a function of time. A standard series of precautions was adopted which greatly reduced the randomness of the kinetic results, although still without yielding satisfactory reproducibility. Samples of S_6 were recrystallized three times, the first time in the presence of sulfur monochloride. In view of the apparent importance of heterogeneous catalysis by basic surfaces all glassware used in these runs was boiled with concentrated hydrochloric acid before use and dried without contact with any basic substance. The six runs shown in Table III were all carried out in this way and in each case the reaction was followed both by triphenylphosphine titration to indicate the per cent. conversion into S_8 and by spectrophotometry to indicate the amount of the intermediate whose absorption is different from that of S_6 or S_8.

TABLE III

CONVERSION OF S_6 TO S_8 OBSERVED BY OPTICAL ABSORPTION AND BY TITRATION

T, 25°; $((C_2H_5)_3N)$, 0.050 M; D_0, 1.40

Run	$(S_6)_0$, g. at./l.	D_{max}	% Reaction at max.	Minutes to max.	First-order k for depolymerization, sec.$^{-1}$ × 10^3
145	0.0192	2.62	11	1.5	5.3
147	.0204	2.56	22	1.75	5.8
148	.0195	2.55	9	1.1	10.4
149	.0187	2.58	27	9	7.1
150	.0190	2.52	22	1.5	6.5
161	.0203	2.92	42	11	(Not first order)

Far from being constant, the optical density showed a steep rise to a maximum which was reached within a few minutes after mixing the sulfur and amine solutions and thereafter declined at a much slower rate. A typical run is shown in Fig. 3, in which optical density is plotted against per cent. conversion to S_8. When titration shows that about 9% of the material has been converted into the final stable form, the optical density has reached its maximum and thereafter increasing conversion to S_8 is associated with a steady decline in optical density. This result is exactly what would be expected if the initial step in the reaction were a polymerization of S_6 to a high polymer similar in character to that produced by irradiation of solutions of ordinary sulfur. Fig. 1 shows that if S* were an intermediate in the conversion of S_6 to S_8 just such a rise and fall of the optical density would be observed.

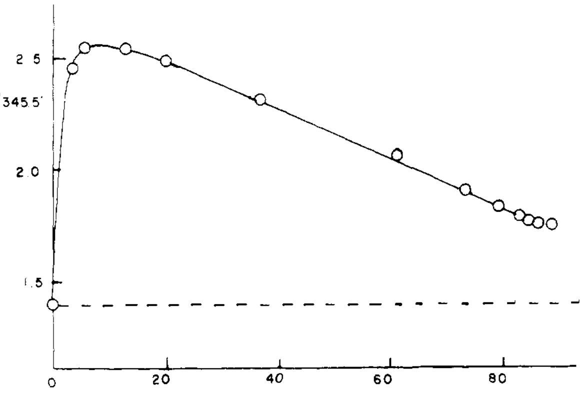

Fig. 3.—Optical density near the isosbestic point of S_6 and S_8, plotted against fraction of conversion to S_8 as determined by titration with triphenylphosphine. Run 148, T, 25°; (Et_3N), 0.050 M.

In these runs the rate of rise of optical density to the maximum varies over a ten-fold range, the maximum absorption occurring at times varying from 1.1 to 11 minutes. The per cent. conversion to S_8 at the point of maximum intermediate formation likewise varies from 9 to 42, but in one respect this set of runs presents a concordance not previously met with in this research. During the period of decline of optical density five out of these six runs show first-order character, a plot of log $(D - D_\infty)$ against time being linear. The values of the first-order rate constant vary by only a factor of two, showing an average of 7.0 × 10^{-3} sec.$^{-1}$ and a mean deviation of 1.4 × 10^{-3} or 20%. Such a plot of the data from run 147 extending over more than 6 half-lives is shown in Fig. 4.

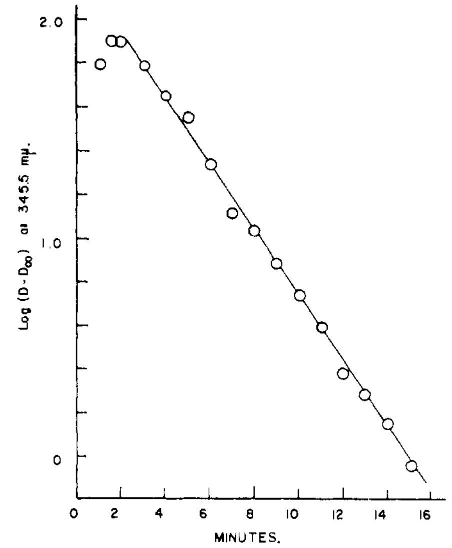

Fig. 4.—Depolymerization stage of conversion of S_6 to S_8 at 25° observed spectrophotometrically (run 147).

Two kinds of tests then suggest themselves to verify that polymeric sulfur is an intermediate in the conversion of S_6 to S_8. If the absorbing intermediate has the character of a high polymer, it should be capable of light scattering in the manner characteristic of high polymers.[7,8] Furthermore, since it is possible to prepare S* independently by irradiating a solution of S_8 in benzene, there should be some correspondence between the behavior of S* reverting to S_8 and that of the conversion of the intermediate to S_8 when this intermediate is formed from S_6.

Through the courtesy of Professor Paul M. Doty, who made his apparatus available to us, two runs were carried out at room temperature in which the conversion of S_6 to S_8 was followed by recording relative values of the light scattered at right angles to the beam. Figure 5 shows a graph of the galvanometer reading as a function of time. The point at zero time is that determined on the reacting solution before the addition of amine. In both of these runs the first stage of the reaction was so fast that the maximum galvanometer deflection had been reached and probably passed before the solutions had been replaced in the apparatus after mixing. It is evident that the same intermediate which is responsible for a rise in optical density in the spectrophotometric runs here produces substantial light scattering, giving evidence of a macromolecular intermediate. For comparison with the optical runs, plots were made of log $(G - G_\infty)$ against time for these light scattering runs. G is the galvanometer reading at any time and G_∞ is the final value. In each run these plots were linear over three half-lives, yielding first-order rate constants of 1.13 × 10^{-2} and 9.8 × 10^{-3} sec.$^{-1}$, within 62 and 40%, respectively, of the average value by spectrophotometry. Figure 6 shows one of these plots.

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(7) P. Debye, *J. Appl. Phys.*, **15**, 338 (1944).

(8) Hj. Staudinger and I. Haenel-Immendorfer, *Makromol. Chem.*, **1**, 185 (1943).

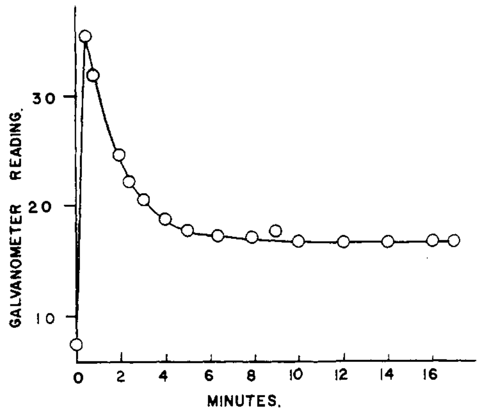

Fig. 5.—Light scattering during conversion of S_6 to S_8.

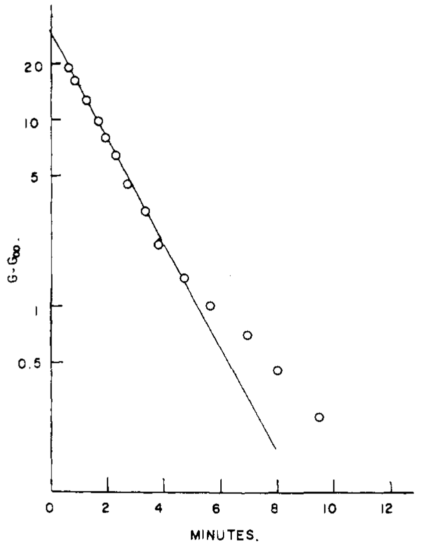

Fig. 6.—Depolymerization stage of conversion of S_6 to S_8, observed by light scattering.

In Fig. 7 are shown four different types of measurement bearing on the depolymerization of polymeric to octatomic sulfur. The curve represented with tilted squares shows the galvanometer reading as a function of time in the light scattering experiment. The open circles represent the measurements of optical density against time in run 147. The level squares represent the course of a titration of fast reacting sulfur in the presence of S_8, also from run 147. The remaining curve (dots) represents a spectrophotometric observation by Dr. Garbis Meguerian of the conversion of irradiated sulfur into S_8. It can be seen that the time scales of all these measurements are as consistent as would be expected with the idea that irradiated sulfur and the intermediates in the conversion of S_6 to S_8 both represent quite similar forms of polymeric sulfur.

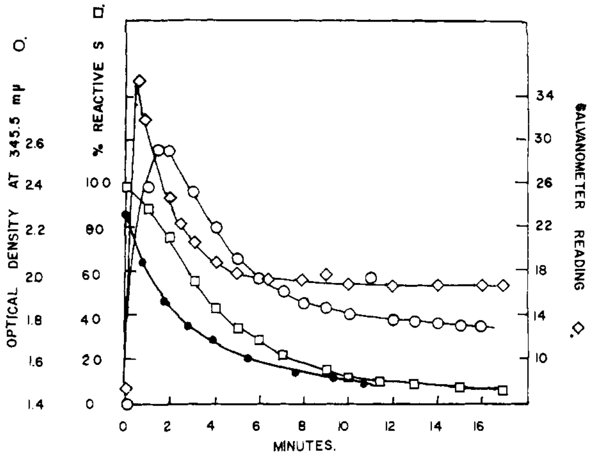

Fig. 7.—Comparison of conversion of S_6 to S_8 observed spectrophotometrically (○), by light scattering (◇), and by titration with triphenylphosphine (□), with depolymerization of photosulfur (●).

Discussion

The general mechanism of conversion of hexatomic to octatomic sulfur—polymerization of the former, followed by depolymerization to the latter—is one which could occur by thermal initiation (spontaneous ring-opening of S_6), by attack of a free radical to form the reactive species $RS_6^{\cdot}$, or by attack of a nucleophilic agent to yield the intermediate RS_6^-. In each case the intermediate would be of a type known to form sulfur–sulfur bonds readily, and thus doubtless capable of rapid attack on further molecules of S_6 to extend the polymer chain. Any stage of this extension beyond the first would yield an ion or radical whose reactive end could attack the eighth sulfur atom from itself and split a cyclic S_8 unit from the chain

$$R^{\cdot} + S_6 \longrightarrow RS_6^{\cdot} \xrightarrow{nS_6} R(S_6)_nS_6^{\cdot} \longrightarrow S_8 + R(S_6)_{n-1}S_4^{\cdot}$$

$$R^- + S_6 \longrightarrow RS_6^- \xrightarrow{nS_6} R(S_6)_nS_6^- \longrightarrow S_8 + R(S_6)_{n-1}S_4^-$$

It would be conceivable that the polymeric material detected by the spectroscopic and light scattering observations might consist entirely of such reactive polysulfide radicals or ions. However, the increase in optical density during the polymerization stage is comparable in magnitude with that when a sample of S_8 is irradiated with a high degree of conversion to fast-reacting sulfur and hence corresponds to the existence of most of the material, not just a small amount, in polymeric form. The reaction at any such stage may be quenched, and the optical density made stable, by adding acetic acid in excess over the amine, indicating that the polymeric substance is not a short-lived one like a free radical. The stable polymeric material in this case is then either a chain with a catalyst unit at one end and hydrogen at the other (RS_xH), or, more probably, cyclic macromolecules of sulfur, formed by reversible cyclization from the reactive intermediate

$$RS_{m+n}^{\cdot} \longrightarrow S_n + RS_m^{\cdot}$$

$$RS_{m+n}^- \longrightarrow S_n + RS_m^-$$

It is a logical hypothesis, as suggested by Krebs,[9] that an amine R_3N might catalyze the redistribution of sulfur, or in the present case the polymerization of S_6, by reversible addition to yield dipolar intermediates.

$$R_3\overset{+}{N}S_x^-$$

Such an intermediate would have the required chemical properties for the present reaction. However, sensitive methods have failed to detect any direct combination between sulfur and triethylamine. The ultraviolet and visible spectrum of S_8 is unaffected by the addition of triethylamine in

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(9) H. Krebs and E. F. Weber, *Z. anorg. allgem. Chem.*, **272**, 292 (1953).

large excess, and the infrared spectrum of triethylamine is similarly unaffected by the addition of octatomic sulfur, despite the known ability of amines to redistribute sulfur from S_8.

Moreover, the extreme variability of the rates of polymerization and depolymerization is a clear indication that the catalysis is not brought about solely by those molecular species whose concentrations have been controlled. We are forced to the conclusion that the actual catalyst of the polymerization is something produced by the action of triethylamine upon some substance present in vastly smaller concentrations than itself. These concentrations are greatest in unrecrystallized S_6 and are reduced by careful purification and probably brought to their lowest point in the presence of iodine.

Sulfite, bisulfite, sulfide, hydrosulfide, polysulfide and hydropolysulfide ions are all known to attack octatomic sulfur at a high rate at ordinary temperatures. In the known instances of triphenylphosphine[5] and cyanide ion,[1] the attack of a nucleophilic reagent upon S_6 is immeasurably faster than upon S_8. We can, therefore, well believe that even traces of these ions might exert a powerful effect upon the polymerization of S_6 and the depolymerization of S^*. Sulfur dioxide, hydrogen sulfide and hydrogen polysulfides all are formed during the acidification of thiosulfate and are, therefore, likely impurities in S_6.[10] We have established that sulfur dioxide alone is not a catalyst for the conversion of S_6 to S_8 but that the addition of sulfur dioxide in a concentration of 2.6×10^{-6} M caused the amine-catalyzed conversion of a sample of S_6 after five recrystallizations to proceed with a half-conversion time of 1.7 minutes, a speed exceeded by only one experiment using raw S_6. Further investigation of this catalysis by traces, together with evidence that more than one such catalyst is involved, will be described in a forthcoming publication.

In view of the limited solubility of the monomeric forms of sulfur the question arises how it is possible for polymeric sulfur to remain in solution during the conversion process. Actually, it is possible to produce a turbidity recognizable as a fine precipitate by irradiating a saturated solution of S_8 in carbon tetrachloride or benzene. It is likely that the light-scattering solutions which occur during the conversion from S_6 to S_8 represent unagglomerated particles of colloidal size rather than a material in reversible solution. Polymer particles of this size are accessible to immediate attack by reagents in solution as can be demonstrated by the instant clearing of a turbid carbon tetrachloride solution by the addition of a small amount of piperidine. Thus, whether the intermediate be regarded as in solution or in suspension, its reactions do not show the lag often characteristic of heterogeneous reactions.

Of the two stages of the reaction which have been observed kinetically, only the second shows convincing adherence to any simple kinetic order. The first-order character of the depolymerization places some limits on the interpretation of the mechanism. The effectiveness of traces of co-catalysts mentioned above might possibly lead us to expect that all of the potential catalyst present either would remain combined with polymer or would attack polymer rapidly and that the rate of appearance of S_8 would be a measure of the concentration of the anion or dipolar ion formed by attack of the catalyst upon the polymer. If both these expectations were correct, the depolymerization would be of zero order during a large part of its course, since there is reason to believe that the catalyst concentration is only a small fraction of that of sulfur itself. Since the depolymerization is in fact of the first order, it is likely that the fraction of the catalyst which is combined with sulfur at any time is proportional to the concentration of reactive sulfur or to the number of S–S links which are not a part of S_8. This would mean that, small as the concentration of catalyst is, only a fraction of the catalyst is actively involved at any time in combination with sulfur. If the particles of S^* are large enough so that the reaction is microscopically heterogeneous then the attack of catalyst upon polymeric sulfur should be at a rate proportional to the surface of the latter, approximating the two-thirds power of polymer concentration. When a high degree of control is achieved over the experimental variables, such kinetics can be distinguished from first order.

One of the striking results of this survey is the lack of correlation between the rates of polymerization and depolymerization when these are carried out continuously starting with any given specimen of S_6. To a degree such a lack of correlation might be anticipated if the first stage were homogeneous and the second stage heterogeneous. However, the large variations observed suggest that not all the reactions are due to the operation of the same catalyst. Sulfide or hydrosulfide ion, after catalyzing the polymerization of S_6, might well be regenerated in its original form or as a polyhydrosulfide ion such as was active in the process. Sulfite or bisulfite ion, on the other hand, would emerge from the process eventually as thiosulfate ion of greatly altered thiophilic activity. These possibilities are also being followed up in our current work.

This survey leads to the conclusion that the complexities of the conversion of hexatomic to octatomic sulfur result from the successive and in part simultaneous polymerization of metastable sulfur and depolymerization to stable sulfur catalyzed by minute amounts of one or more anionic sulfur-containing catalysts. It is an instance, probably unique in polymer chemistry, of a polymerization and depolymerization occurring irreversibly in quick succession under a fixed set of conditions.

Experimental

Preparation of S_6.—The method is that of Aten.[3] After rapid mixing of 300 cc. of concentrated hydrochloric acid and 150 cc. of saturated sodium thiosulfate solution a rapid extraction is carried out with 100 cc. of an organic solvent (benzene, toluene, chloroform and carbon tetrachloride gave similar yields). The dark, reddish-yellow extract, stored in the refrigerator, yields 0.8 to 1.0 g. of reddish-yellow hexatomic sulfur, crystallizing in the rhombohedral system.

The mother liquor, after removal of the crude product at 8°, remained much more intensely colored than a saturated

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(10) R. E. Davis, THIS JOURNAL, **80**, 3565 (1958).

sulfur solution at the same temperature. By evaporation and by triphenylphosphine titration the sulfur content was found to be 23.8 and 23.4 mg. per cc. respectively, whereas the solubility of pure S_6 was found to be 7.2 and of S_8, 10.5 mg. per cc., respectively, at the same temperature. Thus, the yellow extract contains 32% more sulfur than can be accounted for by saturation with both S_6 and S_8. The optical density of this solution was about twice that to be expected from a solution saturated with both S_6 and S_8. The simplest explanation of these results would be that the solution remains long super-saturated with S_8, the isolation of S_6 being made possible by its relatively high rate of crystallization. The residue on evaporation of the mother liquor was only partly crystalline and the absorption of the solution suggested the presence of some polymeric sulfur. However, there can have been relatively little of this species since the cryoscopic molecular weight of the dissolved material determined on a sample of thoroughly water-washed mother liquor (40 washings) was 252, corresponding to $S_{7.9}$.

The crude S_6 was recrystallized from benzene with the addition of one drop of a 0.001 *M* solution of iodine per gram of sulfur. Without this precaution, the hexatomic sulfur underwent polymerization during warming of the solution after a few recrystallizations.

Attempts to substitute sodium benzenethiosulfonate or sodium ethanethiosulfonate for sodium thiosulfate in the preparation of hexatomic sulfur were unsuccessful.

Under the conditions of our standard triphenylphosphine titration[5] (0.01 *M* triphenylphosphine solution in benzene containing 20 vol. % of 95% alcohol) S_6 reacts immeasurably fast and the same is true of the much slower reagent tri-*p*-chlorophenylphosphine.[5] There appears to be no reaction, however, between S_6 and triphenylarsine. Crystalline S_6 is kept in the refrigerator in the dark but is always recrystallized shortly before use since on long standing it undergoes appreciable conversion into polymeric sulfur. A solution in *m*-xylene showed no decrease in its active sulfur content by titration during nine days at 65.6°. This titration would not reveal the formation of polymeric sulfur but only of S_8.

Hexatomic sulfur showed no infrared absorption between 2 and 16 μ. There is some apparent absorption in the neighborhood of 20 μ which, however, was not well resolved, because it lies close to a strong band of carbon disulfide. In no other solvent does S_6 have sufficient solubility to make the observation of this band promising.

Amine Catalysis.—When piperidine is added to an S_6 solution in benzene, the liquid becomes cloudy for a few seconds, then regains its transparency. Evaporation of the solvent yields crystalline S_8. The conversion occurs much more slowly with triethylamine in place of piperidine and still more slowly with pyridine. Triethylamine was used in all the kinetic runs.

Purification of Materials.—The benzene used as a solvent in the kinetic runs was refluxed over metallic sodium and then distilled from sodium. The carbon tetrachloride was treated with excess chlorine in bright sunlight for 2 days, then washed with water to remove chlorine and distilled from phosphorus pentoxide. Triethylamine was distilled from potassium hydroxide under nitrogen.

Conditions of the Kinetic Runs.—The first kinetic runs with triethylamine as catalyst were made in transparent flasks. Reactions proceeded much faster during the day than during the night. Therefore, the use of blackened reaction flasks was adopted as a standard precaution. A series of runs in which the solvent was boiled under nitrogen to remove oxygen and all transfers were made under nitrogen showed no effect of this precaution upon the rate.

Exclusion of Oxygen.—In run 102, which showed a half-time of about 6 minutes, the greatest precautions were taken to exclude oxygen. The hexatomic sulfur was prepared in a carbon dioxide atmosphere with previous degassing of all solvents and solutions. S_6 prepared in this way and recrystallized in the absence of air was dissolved in a little benzene and the solution introduced into a dissolving flask which was directly connected to a three-way stopcock with nitrogen and vacuum lines and sealed to a storage vessel with a sintered glass filter disk sealed in the connecting neck. The solvent was evaporated with an oil pump, some previously degassed benzene was added and the sulfur was redissolved and again evaporated to achieve the greatest possible removal of sulfur dioxide. Finally, a new solution was made by the addition of further boiled benzene and was freed from some polymeric sulfur formed during these operations by filtration through the sintered disk under pressure of nitrogen. A measured amount of this solution was then introduced by pipetting under nitrogen pressure into a reaction vessel constantly swept with nitrogen saturated with the vapor of purified benzene. The pipetting of samples from the completely black reaction flask was also carried out by pressure of nitrogen. Since the result of this run was indistinguishable from that of others where these troublesome precautions were not maintained, no special attention was given to the exclusion of oxygen in the other runs.

Deactivation of Alumina.—Commercial alumina had a powerful catalytic effect on the conversion of S_6 to S_8. It was found that alumina which had been boiled for several hours with dilute hydrochloric acid and dried at 300° was inactive toward S_6. The catalytic activity was, therefore, due to basic material combined with the alumina. Tests showed that both aluminum chloride and boron fluoride were ineffective as catalysts for this conversion.

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