

basic with alcoholic potassium hydroxide and the product recrystallized twice from aqueous ethanol; m.p., 156.6–157.8°.

Triphenylphosphine Sulfide.—The product of a 7-day reaction of triphenylphosphine and sulfur under nitrogen in benzene was recrystallized twice from benzene–ethanol (1:9) giving white crystals, m.p. 163–165°.

Sulfur Preparations. "Recrystallized S₈."—Sublimed U. S. P. grade sulfur from the Mallinckrodt Chemical Works was recrystallized three times from reagent grade benzene in total darkness. It was dried *in vacuo* at 40° for two days over phosphorus pentoxide in total darkness.

"Bacon-Fanelli Sulfur" was prepared by heating sulfur of the above grade at 300° with one-tenth of its weight of magnesium oxide in evacuated sealed tubes for one week.⁹ The opening of the tubes and further recrystallization of the sulfur from purified benzene was conducted on the vacuum line.

Hexatomic Sulfur S₆.—One volume of an aqueous saturated solution of sodium thiosulfate pentahydrate (Mallinckrodt A. R. grade) at 10° was added to two volumes of concentrated hydrochloric acid (du Pont C.P. 36.5–38.0% HCl) at 0°. The immediate precipitate of sodium chloride was rapidly removed by filtration and the filtrate extracted with two volumes of purified cyclohexane. The yellow cyclohexane extract was washed well with water and then stored in fused silica vessels under nitrogen. The S₆ which deposited was recrystallized from toluene or benzene

as needed. Molecular weight determination by freezing point depression in purified benzene gave values of 5.9–6.1 for the number of sulfur atoms per molecule.

The 1:1 adduct of triphenylphosphine and maleic anhydride was prepared as described by Schönberg and Ismail⁸ and recrystallized from benzene.

Titrimetric rate determinations were carried out as described by Bartlett and Meguerian.¹

Spectrophotometric rate determinations were carried out at 344.5 m μ using the Beckman DU spectrophotometer, fitted with a thermostatted cell compartment. Runs with degassing were prepared with the use of special cells like those described by Fraenkel and Bartlett.¹⁵

Spectra were determined on a Cary model 11 M recording spectrophotometer.

Acknowledgments.—We thank the National Science Foundation and the B. F. Goodrich Company for support of this work; the National Science Foundation for a post-doctoral fellowship to Eugene F. Cox, the National Science Foundation and the National Institutes of Health for predoctoral fellowships at different times to Robert Earl Davis.

(15) G. Fraenkel and P. D. Bartlett, *THIS JOURNAL*, **81**, 5589 (1959).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Reactions of Elemental Sulfur. V. Catalytic Effects in the Conversion of Hexatomic to Octatomic Sulfur

By PAUL D. BARTLETT, ALLAN K. COLTER, ROBERT EARL DAVIS AND WILLIAM R. RODERICK

RECEIVED MAY 6, 1960

A method is described for the purification of hexatomic sulfur by washing a benzene solution of it with potassium triiodide, lead acetate and finally potassium hydroxide. Hexatomic sulfur so treated and handled in the absence of air and light is inert to triethylamine for periods from 3000 to 10,000 seconds, after which a slow conversion to polymeric and then to octatomic sulfur occurs. The induction period is eliminated if (a) the experiment is prepared with access of air and light or (b) toluene is used as solvent or (c) small amounts of either hydrogen sulfide or sulfur dioxide are introduced. In the latter cases the rate of polymerization of the purest S₆ is equal to 445 (S₆)(Et₃N)(SO₂) *M*/sec. or to 17,700 (S₆)(Et₃N)(H₂S) *M*/sec. These reaction rates were followed spectrophotometrically at 300 m μ . The enormous variations previously observed in the rate of the S₆–S₈ conversion can be accounted for on the basis of universal contamination of S₆ samples with hydrogen sulfide or sulfur dioxide, which form the highly thiophilic reagents HS[–] and HSO₃[–] in the presence of amines. The same treatment can be applied to the purification of solutions of octatomic sulfur irradiated in benzene, with a reduction of a thousandfold in their rates of conversion into S₈ in the presence of triethylamine. It is concluded that amines do not attack pure hexatomic sulfur directly, as was also shown for pure octatomic sulfur in Part IV.

Introduction

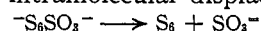
In Part III of this series¹ a preliminary study of the conversion of hexatomic to octatomic sulfur was reported. It was established that this conversion proceeds by way of polymerization of the S₆ followed by depolymerization to S₈. Both stages of the reaction were accelerated by triethylamine. The rates of both stages showed wide variations, uncorrelated with each other, not only from sample to sample but from run to run. In a series of 72 runs similarly prepared, the time of half conversion from S₆ to S₈ varied from 18 to over 60,000 seconds.

It was eventually concluded that minute amounts of such impurities as hydrogen sulfide or sulfur dioxide must be present in all the samples of hexatomic sulfur. This would lead to the formation, in the presence of triethylamine, of small amounts of triethylammonium hydrosulfide or bisulfite, these being the actual catalysts of the S₆–S₈ conversion. This hypothesis suggested special methods of puri-

fication of S₆. In the present work we have applied such methods and have succeeded in preparing hexatomic sulfur with relatively long periods of inertness toward triethylamine. Using these preparations we could in turn confirm the extreme sensitivity of such material to the presence of hydrogen sulfide or sulfur dioxide.

Results

Observations on the Preparation of S₆.—The kinetics of the formation of sulfur from acidified thiosulfate^{2,3} is consistent with a series of displacements of sulfite by thiosulfate ion leading to increasingly long ions of the type HS_xSO₃[–]. As soon as *x* = 6, an intramolecular displacement



can occur through a sterically favored cyclic transition state, leading to hexatomic sulfur. Simultaneous reactions lead to polythionic acid, hydrogen sulfide and polysulfides and other forms of sulfur.

(2) R. H. Dinegar, R. H. Smellie and V. K. LaMer, *ibid.*, **73**, 2050 (1951).

(3) R. E. Davis, *ibid.*, **80**, 3565 (1958).

(1) P. D. Bartlett, G. Lohaus and C. D. Weis, *THIS JOURNAL*, **80**, 5064 (1958).

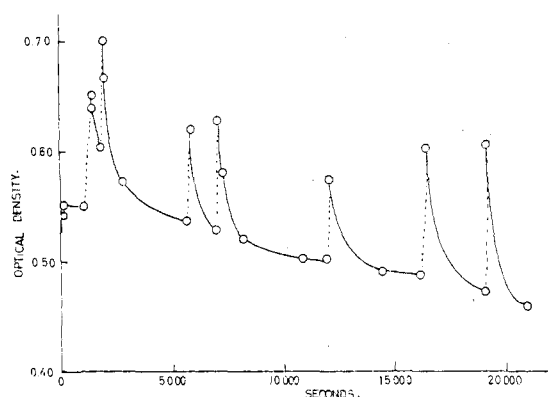


Fig. 1.—Formation of absorbing intermediate during reaction of sulfur solution with sulfur dioxide and triethylamine. At each dotted line a drop of a toluene solution of SO_2 was added to the converted solution of 1.02×10^{-3} g. atm./l. S_8 and 5.50×10^{-3} M triethylamine in toluene; the decline of the baseline indicates conversion of sulfur into thiosulfate; $\lambda = 300 \text{ m}\mu$.

In a series of experiments designed to find the best conditions for preparing hexatomic sulfur, 50 ml. of saturated sodium thiosulfate solution was added to 200 ml. of concentrated hydrochloric acid at temperatures from 0° to -20° , the solution being filtered as rapidly as possible to remove sodium chloride. At various times 50 ml. aliquots of the solution were withdrawn and extracted with 25 ml. of toluene by vigorous mechanical stirring for 40 minutes. The phases were separated and the yields of sulfur determined by isolation and weighing. At each temperature the yield decreased with time, in most cases almost vanishing after 2 hr. The best yield, 16%, was obtained at 0° . The preparations of S_8 were thereafter conducted on the assumption that a temperature not below 0° , together with the most rapid extraction, is advantageous. As implied by the mechanism of Davis³ (which is the microscopic reverse of the formation of thiosulfate from sulfite and sulfur under more basic conditions), the species HS_6SO_3^- can, by two more bimolecular displacements, lead to a precursor of S_8 ; by still further reaction it can yield sulfur species of higher molecular weight. The extraction of the aqueous solutions at an early stage may also preserve the hexatomic sulfur against further ionic attack.

In one preparation of S_8 , the toluene extract was purified by the series of washings described below, examined spectroscopically, and then chilled to -25° with formation of 12% of crystalline S_8 . The optical density, however, in the range 300–350 $\text{m}\mu$ corresponded to an S_8 yield of 63%. Chilling to liquid nitrogen temperature yielded a small amount of viscous product which later solidified, but most of the colored material was recovered only by distillation of the toluene, which left a residue of rubbery sulfur. From these observations it appears that the toluene extract, at least after some hours, has about 80% of its sulfur in the form of species other than S_8 and S_6 .

Spectroscopic Observation of an Intermediate in the Formation of Thiosulfate.—In an experiment

intended for another purpose it was possible to observe the occurrence of a species, probably S_nSO_3^- , as a short-lived intermediate in the reaction of sulfur with sulfur dioxide and triethylamine in toluene solution. Under spectroscopic observation at 300 $\text{m}\mu$, near the isosbestic point of S_8 and polymeric sulfur, the addition of triethylamine to a solution of purified but aged S_8 in toluene caused an immediate rise in the optical density indicating complete reaction of the S_8 . Although further change from polyatomic to octatomic sulfur would cause no further change in the optical density, the addition of a drop of a solution of sulfur dioxide in toluene caused a rapid jump in optical density followed by a rapid decline to a value slightly below that prevailing before the addition. The effect of a series of such additions of sulfur dioxide is shown in Fig. 1. In its over-all result this reaction is a reversal, due to the presence of the amine, of the formation of sulfur from thiosulfate; the temporary increase in absorbancy here resembles the permanent increase brought about by hydrogen sulfide (Part IV).

Purification of Hexatomic Sulfur.—Hexatomic sulfur, prepared as described in Part IV,⁴ was dissolved in benzene and washed successively with water, an aqueous solution of iodine in potassium iodide, aqueous potassium iodide, water, aqueous lead acetate and water. In a final attempt to remove the acidic impurities, the solution was washed with dilute aqueous potassium hydroxide, a process which would have been likely to destroy S_8 if most of the sulfur dioxide and hydrogen sulfide had not already been removed from it. After four washings with water and drying with sodium sulfate, the solution of S_8 was used to prepare kinetic runs.

First Stage of the Conversion, $\text{S}_8 \rightarrow \text{S}^*$.—When the conversion was observed at 348 $\text{m}\mu$, the isosbestic point of S_8 and S_8 , the optical density rose to a maximum and then declined at a rate bearing no discoverable relation to the rate of ascent. Using this wave length, it was possible to follow the second or depolymerization stage of the reaction after the disappearance of S_8 was essentially complete.

In the present work we have adopted the isosbestic point of S^* and S_8 , which occurs at about 300 $\text{m}\mu$, for observation of the initial or polymerization stage of the reaction. At this wave length the optical density rises from the value characteristic of S_8 to that of polymeric sulfur and then undergoes no further change. With hexatomic sulfur which had been recrystallized *in vacuo* and then washed in benzene solution as described above, there was usually an induction period of 3,000 to 4,000 seconds after addition of triethylamine during which no change was observed in the optical density at 300 $\text{m}\mu$. From one sample of S_8 two solutions were prepared and followed kinetically in the presence of 0.0614 molar triethylamine. The solution containing 1.37×10^{-3} gram-atoms per liter of S_8 showed an induction period of 3,500 seconds, while that containing 9.1×10^{-4} gram-atoms per liter of S_8 showed an induction period of 7,500 seconds.

(4) Part IV, P. D. Bartlett, E. F. Cox and R. E. Davis, *ibid.*, 83, 103 (1961).

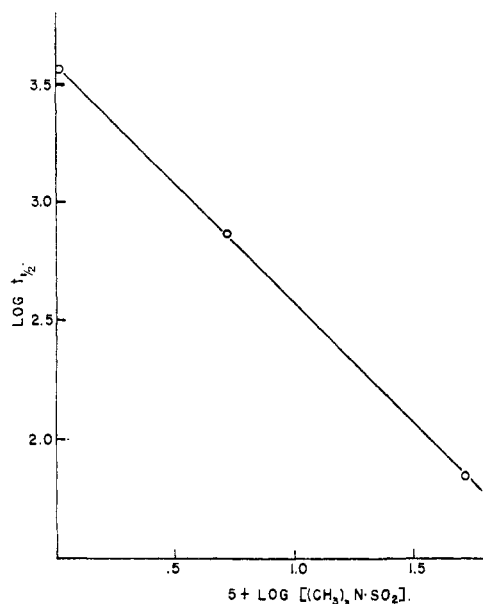


Fig. 2.—Effect of additions of sulfur dioxide (as its complex with triethylamine) on the triethylamine-catalyzed polymerization of hexatomic sulfur in benzene at 25°.

In every case, possibly as a result of slight photochemical reaction during the spectrophotometric observation, conversion to polymeric sulfur eventually began, and the half times of such conversion varied from 3,200 to 17,400 seconds. It appeared that freedom of any solution of S_8 in benzene from co-catalytic impurities was only a temporary matter and that either sulfur dioxide or hydrogen sulfide is always generated in such solutions after a time. In experiments in which toluene instead of benzene was used as the solvent, no induction period was noted, and the polymerization was relatively fast (half time less than 10 seconds). In view of the obviously small amount of impurity which is necessary to bring about the polymerization, it would not be surprising if toluene contained sufficient peroxide to produce catalytic sulfur dioxide rapidly from S_8 or if the side-chain hydrogen of toluene were sufficiently active to form minute amounts of co-catalytic mercaptan from the S_8 .

Co-catalysis by Sulfur Dioxide or Hydrogen Sulfide.—The induction periods achieved by this method of preparation are long enough to permit the quantitative determination of the effectiveness of co-catalysts purposely introduced into the purified hexatomic sulfur. Sulfur dioxide was added as the crystalline trimethylamine-sulfur dioxide complex. In this series of reactions the initial hexatomic sulfur concentration was 1.58 – $1.82 \times 10^{-4} M$, and the triethylamine concentration $4.09 \times 10^{-2} M$ in benzene. All runs were degassed, and controls with only amine added were run on each sulfur solution. Solutions which had induction times in the controls of less than 3,500 seconds were rejected. The results are listed in Table I and shown graphically in Fig. 2.

To test the effect of hydrogen sulfide as a co-catalyst in the polymerization of hexatomic sulfur, stock solutions of the gas in benzene were prepared and diluted. Because of the high vapor pressure of

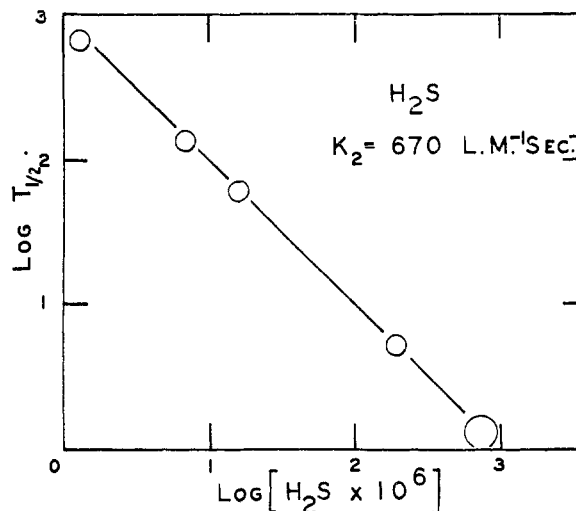


Fig. 3.—Effect of additions of hydrogen sulfide on the triethylamine-catalyzed polymerization of hexatomic sulfur in benzene at 25°.

benzene solutions of hydrogen sulfide, it was difficult to assure reliable concentrations, and the results below $10^{-6} M$ were not reproducible. However, as shown in Table II and Fig. 3, the rates were proportional to the hydrogen sulfide concentration at least over a hundredfold range. All runs were carried out using vacuum technique, with careful degassing of the sulfur and amine solutions.

TABLE I

EFFECT OF SULFUR DIOXIDE (AS TRIMETHYLAMINE COMPLEX) ON THE POLYMERIZATION OF S_8 IN BENZENE AT 25° (Triethylamine $4.09 \times 10^{-2} M$)		
$(CH_3)_3N \cdot SO_2 \times 10^3 M$	$t_{1/2}$ sec.	$k_1/(SO_2)$, l./m. sec.
1.04	3700	17.9
5.22	735	18.0
52.2	71	18.6

TABLE II

EFFECT OF HYDROGEN SULFIDE AS A CO-CATALYST IN THE POLYMERIZATION OF S_8 IN BENZENE AT 25° (Triethylamine, $3.81 \times 10^{-2} M$)		
(H_2S) , $M \times 10^6$	$t_{1/2}$, sec.	$k_1/(H_2S)$, l./m. sec.
0.143	700	692
0.715	150	645
1.58	64	684
18.6	9 ± 4	
158.0	<0.5	

Co-catalyst Depletion and Generation.—In all the experiments of Tables I and II a decrease in rate was observed with time. Decrease in the concentration of sulfur dioxide during this process is inevitable, since it is converted into thiosulfate. It is not so clear how hydrogen sulfide can be lost in a degassed system; perhaps a terminal negatively charged sulfur atom is less catalytically active when embedded in a polysulfur molecule of higher molecular weight than it is in its original form. These results with co-catalyst purposely added suggest that when, as was often the case, S_8 was observed to undergo polymerization with sustained first order kinetics, it was the result of compensating catalyst consumption and catalyst generation

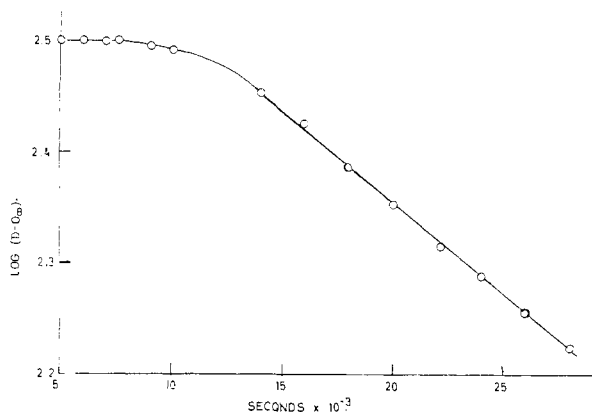


Fig. 4.—Induction period in reaction of purified S_8 in benzene solution with triethylamine. There is no reaction until 7,500 seconds in this experiment, but by 15,000 seconds the sulfur is reacting at a constant rate with apparent first order kinetics; $[S_8] = 9.1 \times 10^{-4}$ g. atom/l.; $[Et_3N] = 6.14 \times 10^{-2}$ M; $\lambda = 300$ m μ .

through reaction of sulfur with the solvent or, in the special cases where access of air was permitted, with dissolved oxygen. Figure 4 shows a typical example of a run with highly purified S_8 having an induction period of 7,500 seconds. The course of the reaction from 13,000 to 28,000 seconds is that of a first order reaction. This rate (half-time, 18,600 sec.) could be produced by a steady-state concentration of 5.5×10^{-8} M hydrogen sulfide (one molecule in 17,500 atoms of sulfur) or of 2×10^{-6} M sulfur dioxide (one molecule in 480 atoms of sulfur).

It was emphasized in Part IV⁴ that, no matter how thoroughly octatomic sulfur was purified, solutions of it which stood in light or air quickly generated substances with co-catalytic properties rendering the reaction of the sulfur with triphenylphosphine amine-sensitive. Figure 5 shows that hexatomic sulfur has this property at least in equal measure. A solution of hexatomic sulfur which had received the full extraction treatment was divided into two parts; one was brought into reaction with triethylamine without the exclusion of light and air, while a solution was prepared from the other identical in composition but with the usual vacuum line precautions. The latter solution showed an induction period of about 4000 seconds, the former began to polymerize immediately.

The Isobestic Point of S_6 and S_8 .—Some of the earlier observations indicated that the optical density of a converted solution did not return to the predicted value, and we have therefore carried out a series of runs in which S_6 was converted to S_8 with 1–2 drops of triethylamine in 85–115 ml. of dry benzene, the initial and final spectra being scanned in the vicinity of 350 m μ to determine at what point the optical densities were identical. The S_6 used for this purpose was recrystallized from toluene between 35 and -25° but was not subjected to the washing procedure. Four experiments with access of air yielded values of 348.3, 349.5, 347.9 and 348.3 m μ for the isobestic point, and a fifth experiment in which all oxygen had been swept out with dry, prepurified nitrogen gave a value of 348.8 m μ ,

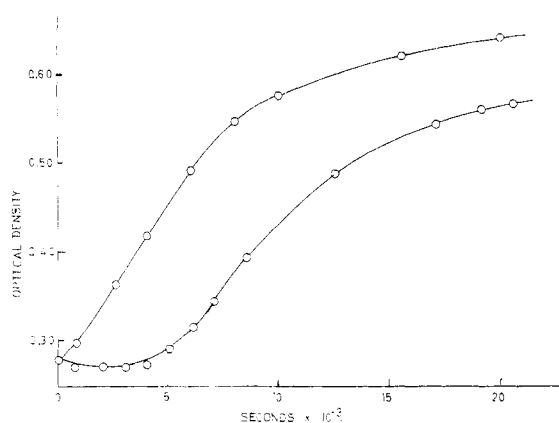


Fig. 5.—Effect of exposure to air on rate of conversion $S_6 \rightarrow S_8$. For both curves, $[S_6] = 1.37 \times 10^{-3}$ g. atom/l.; $[(C_2H_5)_3N] = 6.14 \times 10^{-2}$ M. Lower curve, solution degassed; upper curve, solution exposed to air; $\lambda = 300$ m μ .

the average of the five being 348.6 m μ . The final spectra in these experiments were those of normal octatomic sulfur. It seems likely that the residual absorption in earlier experiments can be attributed to unusually large contamination with hydrogen sulfide, a catalyst which is not consumed and which, in the presence of triethylamine, substantially increases the light absorption of a sulfur solution (Part IV,⁴ Fig. 6).

In determining the spectrum of S_8 , it was discovered that considerable variations between observations made at different times could be eliminated by the inclusion of some triethylamine in the solution. Since irradiation polymerizes S_8 , this observation indicates that the variations may have been due to this cause, the amine serving to re-equilibrate S^* with S_8 .

The Depolymerization Stage.—In Part III¹ it was remarked that in a set of supposedly identical experiments the rate of the depolymerization stage in the S_6 – S_8 conversion varied less wildly than the rate and kinetics of the polymerization stage. In the presence of 0.050 M triethylamine the depolymerization was of the first order in S^* (in g.-at./l.) in five out of six determinations, with an average rate constant of 7.0×10^{-3} sec.⁻¹. Similar rates and kinetics were observed for the return of photo-sulfur to S_8 , supporting the idea that the sulfur formed by irradiation of a solution of S_8 in benzene was similar chemically to the intermediate polymeric species in the S_6 – S_8 conversion. In the light of the results here reported, it would be suspected that the reason for this relative consistency in results is that late in an S_6 – S_8 conversion the co-catalysts in different samples have approached a common level: sulfur samples which contained an abnormally high concentration of hydrogen sulfide or sulfur dioxide had lost some by oxidation or conversion to thiosulfate or escape to the atmosphere; while samples with abnormally little of these contaminants had had time to generate some and establish the steady state indicated in results like those of Fig. 4. It remained to be established that the depolymerization of polymeric and photo-sulfur was subject to the same co-catalysis as the polymerization of S_6 . Since the polymerization and

depolymerization stages can be well separated in time, we have continued to observe the second stage of the reaction by following the optical density at the isobestic point of S_6 and S_8 . It proved easy to dispel the illusion of reproducibility of the rates of depolymerization, although most runs observed at $348\text{ m}\mu$ closely approached first order after the peak absorbancy was passed. Before the introduction of the extraction technique for purification of hexatomic sulfur, there was little correlation between the number of recrystallizations of the starting material and the reaction rate observed. We quote, however, in Table III, a series of eight experiments performed with the same sample of S_6 , which had been recrystallized ten times from toluene and washed twice with benzene and was then stored in the freezer at -25° except when being opened for the preparation of a run.

TABLE III
DEPOLYMERIZATION STAGE OF CONVERSION OF S_6 TO S_8 IN
BENZENE AT 25.13° (SINGLE SAMPLE OF S_6)

Age of S_6 sample, days after crystalliza- tion	Triethylamine, $M \times 10^4$	k_1 , sec. ⁻¹ $\times 10^8$	$k_1/(\text{Et}_3\text{N})$, l./m. sec. $\times 10^6$
0	5.51	22,700	41,200
1	5.51	10,100	18,300
8	4.07	412	1,010
11	8.14	875	1,080
11	8.14	648	797
16	8.14	270	332
61	8.36	612 ^a	732
64	8.36	2	2.4

^a Rate dropped off sharply to about 10% of this value after about half reaction.

In this series the correlation with elapsed time since the recrystallization of the sulfur is unmistakable, even though far from uniform. It seems that on every disturbance of the S_6 crystals some volatile co-catalyst was lost. From our later observations we suspect that any solvent which, like toluene, can form a peroxide in air must be avoided in the treatment of sulfur if the highest degree of freedom from sulfur dioxide is to be achieved.

Pyridine was also investigated as an agent for the S_6 - S_8 conversion; the rates using it were lower than with triethylamine, the depolymerization was uniformly of the first order, but the rate constants, using S_6 without the extraction procedure, were still not reproducible.

Experiments with Photosulfur.—The polymeric nature of photosulfur is shown in several ways. Its solutions scatter light, with a single maximum in the plot of scattering intensity *vs.* angle of scatter.⁵

A 0.01 M solution of ordinary sulfur in benzene had a relative viscosity of 1.010 at 25° , which was increased to 1.046 in 20 minutes' exposure to light at 25,000 foot-candles. When the solution stood in glass in the dark at 25° , the viscosity returned at an accelerating rate to its original value, the return being 89% complete after 48 hr.

The isobestic point of S_8 and photosulfur is not a fixed point like that of S_8 and S_6 but varies some-

what with the manner and degree of irradiation of the sulfur. With a medium-pressure mercury arc the isobestic point moved uniformly from 312 to $319\text{ m}\mu$ as the photopolymerization progressed, whereas in previous comparisons the isobestic point has appeared closer to $305\text{ m}\mu$, with irradiation by sunlight. In most cases the degree of conversion of S_8 to polymeric sulfur was not determined, although this can be done accurately by the triphenylphosphine titration method of Part I.⁶

In a series of 8 experiments solutions of photopolymerized sulfur in benzene were observed in the presence of triethylamine concentrations varying from 2.18×10^{-4} to $1.82 \times 10^{-6}\text{ M}$. The rate constants equivalent to those in the last column of Table III varied from 0.85 to 7.31 l./mole sec., the *smallest* thus being *twice as great as the largest* in Table III. In solutions of photosulfur hydrogen sulfide can often be smelled, and one can easily guess that the higher rate and greater consistency of these results are due to the formation of hydrogen sulfide and possibly thiophenol in minute but catalytically important and reasonably constant proportion to the polymeric sulfur produced.

To test this explanation, a freshly irradiated solution of sulfur in benzene was subjected to the series of washings (iodine, lead acetate, potassium hydroxide) which had proved effective in deactivating hexatomic sulfur. Parallel experiments were conducted on treated and untreated portions of the same photosulfur solution. In each reacting solution the sulfur concentration was $9.65 \times 10^{-4}\text{ M}$, based on octatomic sulfur, and the diethylamine concentration was $1.12 \times 10^{-2}\text{ M}$. The half-times of reaction for the untreated and treated solutions, respectively, were 36 and 92,000 seconds, a difference of more than a thousand-fold. Judging from the total optical density change in the treated solution, the purification method had not removed more than 10% of the photosulfur. Therefore, the depolymerization stage of the S_6 - S_8 conversion is similar to the depolymerization of photosulfur, and both are brought about by the same catalysts as the polymerization stage. Whether an S_6 molecule is being added to, or an S_8 molecule eliminated from, the intermediate polymer, the reaction step is a nucleophilic displacement of sulfur on sulfur and occurs in a negative ion of the type XS_7^- . Under catalysis by a tertiary amine, X is generally $\text{R}_3\text{NHO}_3\text{S}$ or R_3NHS .

Discussion

The evidence is now fairly complete as to the anionic character of the catalysis in the conversion of S_6 to S_8 or of photosulfur to S_8 , and its close relation to the processes involved in the stepwise conversion of sulfur into thiosulfate, thiocyanate and triphenylphosphine sulfide, as well as the formation of S_8 from thiosulfuric acid. Still a number of questions remain unanswered. We have not established, in particular cases, whether the microcontaminant responsible for the sensitization of sulfur to amines is hydrogen sulfide, sulfur dioxide or a mercaptan. By studying sulfur dioxide in the form of its stable trimethylamine complex, we may

(5) Unpublished observation by Jon B. Applequist of this department.

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

have considerably underestimated its power as a co-catalyst of the S_6 polymerization; from the properties of this compound it is probably less dissociated into free sulfur dioxide than the corresponding complex with triethylamine which would otherwise determine the SO_2 level in the solution. It is an indication in this direction that in the triphenylphosphine reaction described in Part IV, where sulfur dioxide was introduced as such and not as an amine complex, it appeared to be a stronger co-catalyst than hydrogen sulfide and not a weaker one, as here.

Another unanswered question concerns the molecular state of the polymeric sulfur which is intermediate in the S_6 - S_8 conversion. Since the elimination of S_8 from a polysulfur chain is a series of attacks of the negatively charged chain end on sulfur atom No. 8 in the chain, this process could, of course, happen directly in competition with the chain growth. In such a case, however, we should expect a simple proportionality between polymerization and depolymerization rate with any one catalyst, something which is not observed. There are at least two obvious steps that might prolong the life of the intermediate polymeric sulfur. One is the formation of cyclic S_n molecules by displacement of $S_2O_3^{2-}$ from the end of the ion $-O_3S-S_n-S^-$, while another is reaction of the S^- end of the same ion with sulfur dioxide to yield a sulfane- α -thionate- ω -thionite. Only the former process would have any counterpart in an H_2S -catalyzed conversion. It may be significant that in the case of photosulfur, where hydrogen sulfide is known to be present, the purification procedure did not produce a period of total inertness to triethylamine, but only a greatly diminished rate of depolymerization. This can be understood if some of the photosulfur molecules are terminated by hydrogen atoms abstracted from the solvent, being thus in fact molecules of polysulfane rather than of sulfur.

It would be interesting to determine experimentally the heat and entropy of polymerization of hexatomic sulfur. Ordinary sulfur⁷⁻⁹ exhibits a

(7) R. E. Powell and H. Eyring, *THIS JOURNAL*, **65**, 648 (1943).

"floor" instead of the usual "ceiling" temperature for polymerization.¹⁰ According to Gee,⁸ the polymerization of S_6 (unlike S_8) is exothermic to the extent of 5 kcal./mole, based on liquid S_6 ; accordingly it cannot have a floor temperature. If, as seems likely, polymerization of S_6 is attended by an entropy increase, it cannot have a ceiling temperature either, and hexatomic sulfur will be polymerizable at all temperatures. This is consistent with the long-standing failure to discover any direct way of preparing it from other forms of sulfur.

Experimental

Sulfur Preparations.—Hexatomic sulfur, S_6 , was prepared as previously described.⁴ It was subjected to the special purification procedure described below.

Photo-sulfur, S^* .—Sulfur solutions (0.01 M S_8) in benzene were irradiated in quartz tubes with the light from a CH-3 Hanovia medium-pressure mercury arc operated at 450 volts. These samples were used for dilution and kinetic study of the depolymerization rate.

Purification Procedure.—Solutions of hexatomic sulfur in benzene or cyclohexane or freshly irradiated solutions of octatomic sulfur in benzene were subjected to these extractions:

water	3 times
aqueous KI,	until a light pink color remained in the benzene layer
fresh concd. aqueous KI	4 times
water	3 times
dilute aqueous $Pb(OAc)_2$	twice
filtration	if necessary
water	3 times
dilute aqueous KOH	once
water	4 times

The solutions were then dried with sodium sulfate, diluted to an appropriate concentration as determined by optical density at 300 $m\mu$, degassed and used immediately. From the limited lengths of the induction periods it appeared that these solutions always generated catalysts and could accordingly not be stored.

Kinetic procedure was the same as described for the runs with exclusion of air in Part IV.⁴

Acknowledgment.—This work was generously supported by The B. F. Goodrich Company.

(8) G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952).

(9) F. Fairbrother, G. Gee and G. T. Merrall, *J. Polymer Sci.*, **16**, 459 (1955).

(10) F. S. Dainton and K. J. Ivin, *Nature*, **162**, 705 (1948); *Trans. Faraday Soc.*, **46**, 331 (1950).