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Reactions of Elemental Sulfur. IV. Catalytic Effects in the Reaction of Sulfur with Triphenylphosphine

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Benzene solutions of triphenylphosphine, kept in light in a limited oxygen supply, form a product which (1) causes strong autocatalysis in subsequent reaction with sulfur; (2) is destroyed at the boiling point of benzene or in the presence of excess oxygen. A spectrum has been determined which is thought to be that of the triphenylphosphinium cation radical; this species, however, could not be produced by illumination in rigid media and is much more fugitive than the tri-*p*-tolylammonium cation radical. Sulfur dioxide is a weak catalyst, and the triphenylphosphine-maleic anhydride adduct a strong one, for the formation of triphenylphosphine sulfide. Triethylamine appears as a strong but not reproducible catalyst for the reaction of ordinary sulfur with triphenylphosphine. Increasingly careful purification of the sulfur, together with handling of all solutions in the dark, has yielded a set of kinetic results in which 0.027 *M* triethylamine increases the reaction rate by only 6%, contrasted with 45-fold for an earlier sample of sulfur and set of conditions. It is found that hydrogen sulfide and sulfur dioxide are powerful co-catalysts with triethylamine; as little as 3 molecules of the former, or one molecule of the latter, in 75,000 atoms of sulfur will produce an observable effect. It is concluded that triethylamine itself does not attack sulfur or catalyze its reactions but that the effects observed are due to triethylammonium sulfide, hydrosulfide and sulfite. The mechanism of the co-catalysis is discussed. Hexatomic sulfur has 25,000 times the reactivity of octatomic sulfur toward triphenylphosphine in benzene at 7.35°, where its reaction rate was measured.

Introduction

Freshly prepared solutions of triphenylphosphine react with solutions of ordinary sulfur (S_8) in organic solvents at a reproducible rate with second-order kinetics to yield triphenylphosphine sulfide.¹ The reaction responds to ionizing solvents in the same way as the Menschutkin reaction, and the effect of substitution in the phenyl groups (Hammett $\rho = -2.5$) also indicates that the rate is controlled by nucleophilic attack of triphenylphosphine upon the sulfur ring.

In contrast to this clear picture are a number of puzzling catalytic phenomena which appear on closer investigation of this reaction. These are the subject of the present paper.

Results

Effect of Aging of Solutions on the Uncatalyzed Reaction.—A solution of triphenylphosphine in benzene, on standing in air, forms triphenylphosphine oxide at a rate corresponding, in our solutions, to about 20% in five days. This oxidation is cut down to about 7% by hydroquinone at saturation and to about 4% by 1 mole % of *t*-butylcatechol. Triphenylphosphine oxide, even added to the extent of 50 mole per cent. based on the triphenylphosphine, has no influence on the rate or kinetic form of the reaction between triphenylphosphine and sulfur. However, if the benzene solution of triphenylphosphine is kept under ordinary tank nitrogen for several days (without degassing treatment) in laboratory light and then brought into reaction with sulfur, the rate of reaction (as followed by titration) shows a rapid acceleration from an initial normal value. Figure 1 shows the second-order plots of typical kinetic runs with fresh solutions of triphenylphosphine and with those aged for different intervals before reaction.

This pronounced autocatalytic effect can be eliminated in several ways: (1) by aging the solution in the dark instead of in the diffuse light of the laboratory; (2) by aging under air or oxygen, in the light; (3) by complete degassing of the solution before aging; (4) by inclusion of 1 mole % of *t*-

butylcatechol; (5) by heating the benzene-triphenylphosphine solution under reflux for 20 minutes between the aging and the rate measurement. The same aging result can be produced in less than an hour by direct sunlight, as in four days in diffuse light. These statements summarize the results of 57 titrimetric and 19 spectrophotometric rate experiments under systematically varied conditions.

We believe that these results lead uniquely to the interpretation that in an oxygen-deficient atmosphere triphenylphosphine, under photoexcitation, yields a long-lived but reactive product (possibly a peroxide) which is destroyed at the boiling point of benzene, reacts with excess oxygen to form triphenylphosphine oxide, but survives under limited oxygen supply. This compound must react with sulfur during the period of kinetic observation to yield a product which in turn is a catalyst for the reaction of sulfur with triphenylphosphine.

Two tests suggested by the idea of an intermediate peroxide or "moxide" resulted negatively. Solutions of triphenylphosphine which gave autocatalytic reactions with sulfur did not show the presence of peroxide when treated either with acid-potassium iodide solution or with ferrous sulfate-ammonium thiocyanate reagent. A solution of triphenylphosphine in di-*n*-butyl ether absorbed oxygen slowly to yield triphenylphosphine oxide without any induced peroxidation of the ether.

Similar aging treatment of the sulfur solutions prior to reaction is without effect upon the kinetics.

The attack of a peroxide upon excess sulfur could lead to a complicated series of products. The most obvious of these, sulfur dioxide, is a strong electrophilic reagent and might be expected to affect the sulfur-triphenylphosphine reaction in the same way as the addition of phenol,¹ also an electrophilic solute.² This could be shown to be the case; the addition of 0.0012 *M* sulfur dioxide to a kinetic run containing 0.0120 *M* triphenylphosphine and 0.0240 g. at./l. sulfur increased the observed second-order

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

(2) For a discussion of phenols in the role of Lewis, rather than Brønsted, acids, see P. D. Bartlett and H. J. Dauben, Jr., *ibid.*, **62**, 1339 (1940).

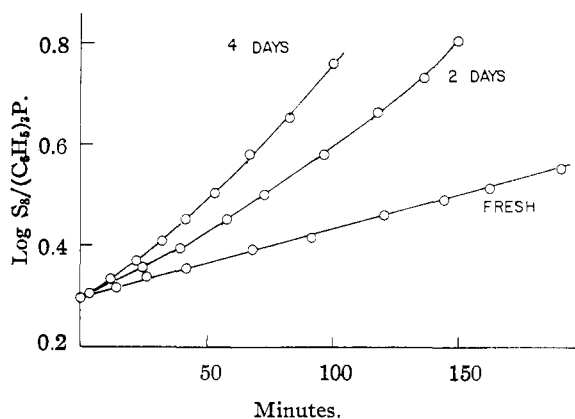


Fig. 1.—Effect of aging of triphenylphosphine solution (in diffuse light under nitrogen without degassing) on rate of reaction with sulfur in benzene at 25°.

rate constant from the normal 4.34 to 6.0×10^{-3} l./mole sec. Thus, generation of sulfur dioxide in amounts to be expected from the rate of deterioration observed for triphenylphosphine would produce the type of autocatalysis which is seen.

The Action of Light on Triphenylphosphine.—Our pure triphenylphosphine was kept in a vacuum desiccator in a dark cupboard. When it was taken out into the light, a pink color appeared on those crystal surfaces which were toward the light source. Triphenylphosphine crystals would turn dark pink in five minutes' exposure to direct sunlight. The pink color was discharged during about five minutes' exposure to air, after which the cycle could be repeated.

These color phenomena are reminiscent of the experience of Ramirez and Dershowitz,³ who showed that the immediate reaction between triphenylphosphine and chloranil, which produced a red color, was also attended by the development of paramagnetic resonance absorption, consistent with the presence of the triphenylphosphinium cation radical, $(C_6H_5)_3P^{\cdot+}$. Such a radical could be involved in the photoexcitation of triphenylphosphine, an excited molecule donating an electron either to an oxygen molecule or to a molecule of the solvent benzene or even to a second molecule of triphenylphosphine, the most likely possibility in the crystal. We irradiated some triphenylphosphine in rigid glasses of methylpentanes and ether-pentane-alcohol at 77° K., but no absorption resulted corresponding to that which has been observed in tri-*p*-tolylamine.⁴ Oxidation of triphenylphosphine with iodine and silver perchlorate, conditions which convert tri-*p*-tolylamine into tri-*p*-tolylaminium perchlorate,⁵ yielded no crystalline product but a rapidly fading color and a residue which reacted with oxygen to form a brown amorphous product.

Molecular Complexes of Triphenylphosphine.—With triphenylphosphine and chloranil under the conditions of Ramirez and Dershowitz, modified only by the use of ether instead of benzene as

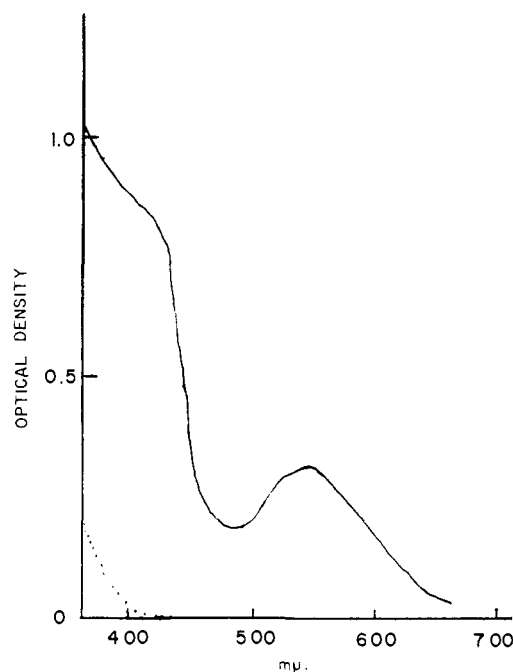


Fig. 2.—Spectrum of reaction product between triphenylphosphine and chloranil in ether solution. Lower curve immediately after mixing; upper curve after 2000 seconds.

solvent, a rapid homogeneous reaction was observed in which the dark pink color lasted long enough for determination of its spectrum (Fig. 2). In the course of time the band centered near 550 $m\mu$ disappeared leaving the band at 390–400 $m\mu$ which is characteristic of the tan-yellow adduct of triphenylphosphine and chloranil.

Like chloranil, 1,3,5-trinitrobenzene yielded a deep red product with triphenylphosphine in solution in ethanol or chloroform. The red solid which separated, however, was not a 1:1 adduct and did not depress the melting point of trinitrobenzene on admixture. This solid was not a catalyst for the reaction of triphenylphosphine with sulfur.

The brown 1:1 adduct of triphenylphosphine and maleic anhydride,⁶ crystals with a distinct odor of ozone, proved to be a strong catalyst for the triphenylphosphine-sulfur reaction. The presence of 1 mole % of this adduct, based on the triphenylphosphine reacting, afforded a second order rate constant about 20 times as great as that of the uncatalyzed reaction. Nevertheless, the rate was normal when only maleic anhydride was added to the reacting solution and also in the presence of 1 mole % of adduct and 10 mole % of maleic anhydride. If this catalysis is actually due to the adduct itself, we may speculate that the adduct has the structure of a dipolar ion, which may produce an increase in the ionizing power of benzene similar to the large effects of lithium perchlorate in ether observed by Winstein, Smith and Darwish.⁷ (According to the equations of those authors, a concentration of salt corresponding to our 0.000122 M adduct produced a 40-fold increase in the rate of

(3) F. Ramirez and S. Dershowitz, *THIS JOURNAL*, **78**, 5814 (1956); *Chem. and Ind.*, 1956, 865.

(4) G. N. Lewis and D. Lipkin, *THIS JOURNAL*, **64**, 2801 (1942).

(5) S. Granick and L. Michaelis, *ibid.*, **62**, 2241 (1940).

(6) A. Schönberg and A. F. A. Ismail, *J. Chem. Soc.*, 1374 (1940).

(7) S. Winstein, S. Smith and D. Darwish, *THIS JOURNAL*, **81**, 5511 (1959).

ionization of *p*-methoxyneophyl tosylate in ether solution.) The counter-effect of excess maleic anhydride is obscure. The simple alternative explanation suggested by the ozone odor of the adduct is unlikely, since even if ozone were present in an amount equivalent to the adduct it could not produce enough sulfur dioxide to have the observed powerful catalytic effect.

Catalysis by Triethylamine.—It was first observed by Meguerian⁸ that the triphenylphosphine-sulfur reaction was strongly catalyzed by small amounts of triethylamine or tri-*n*-butylamine. Such catalysis was then considered to be one more example of the universal activity of basic substances in promoting the redistribution of sulfur. Further investigation showed that this catalysis had some very unusual characteristics. Linear in amine at low concentrations, it showed a "saturation" effect; no further increase in rate could be produced above 0.027 *M* amine (45 times the uncatalyzed rate). It was shown that no appreciable amount of any complex was formed between sulfur and triethylamine at these concentrations; such a mixture showed only the normal infrared spectrum of triethylamine and the normal ultraviolet and visible spectrum of octatomic sulfur.

Next it appeared that the saturation effect could be observed by different investigators, the rates being reasonably consistent within a series of identically performed experiments but not from one series to another. In 75 kinetic experiments, followed spectrophotometrically, the irreproducibility as well as the rate was generally increased by the presence of air or light, increasing concentration of amine or standing of either sulfur or triphenylphosphine with triethylamine before the beginning of the kinetic measurement.

Experiments in Total Darkness.—With these results as a guide, a series of experiments was carried out in a totally darkened laboratory. All purifications were performed in darkness and vacuum-line work was done using a 15-watt red safe-light. All solutions for kinetic experiments were kept in the dark and transported in photographic changing bags. At five amine concentrations, up to 0.0681 *M* amine, the rate was followed both in air and with total degassing. In the dark, with freshly prepared solutions, the presence of air was without effect on the rate; but an amine concentration (0.027 *M*) which in the earlier experiments had given 45 times the uncatalyzed rate now gave only 1.67 times the uncatalyzed rate. Over the range of amine concentration used, the rate constant was a linear function of the amine concentration.

Since these results suggested that the catalytic power of triethylamine was rapidly approaching zero as the conditions became cleaner, an attempt was made to produce some rigorously acid-free and organic-free sulfur by the method of Bacon and Fanelli.⁹ With this material the highest concentration of triethylamine used, 0.0680 *M*, gave a rate constant only 9% higher than that in the absence of amine. The results of these series of experiments are shown in Table I. Figure 3 shows graphically

(8) G. Meguerian, unpublished work in this Laboratory.

(9) R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

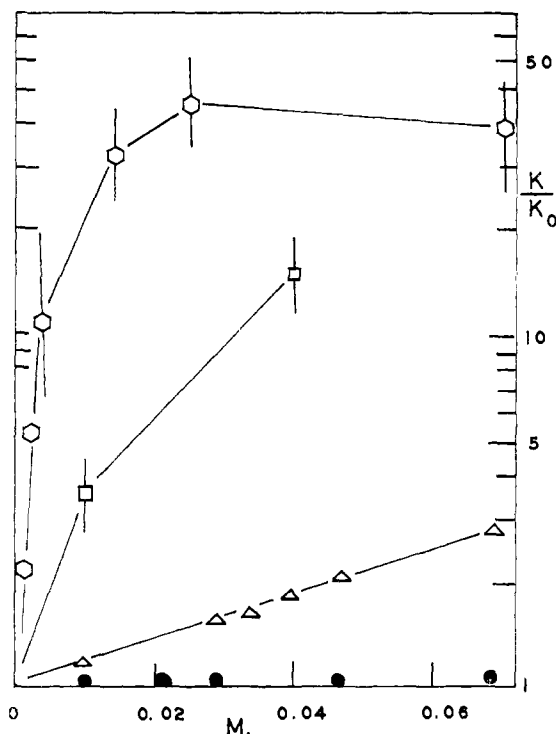


Fig. 3.—Triethylamine catalysis of reaction between triphenylphosphine and sulfur in benzene at 25°: ○ and □, different samples of sulfur, solutions prepared in light; △, recrystallized sulfur, solutions prepared in total darkness; ●, "Bacon—Fanelli" sulfur, solutions prepared in total darkness.

these results together with those of two preceding series on catalysis by triethylamine.

TABLE I
EFFECT OF TRIETHYLAMINE ON REACTION RATE OF TRIPHENYLPHOSPHINE WITH PURIFIED SULFUR IN BENZENE AT 25° IN TOTAL DARKNESS

Amine, <i>M</i>	10 ³ <i>k</i> ₂ ^a for recrystallized S ₈ ^b			10 ³ <i>k</i> ₂ ^a for Bacon—Fanelli S ₈ ^b		
	Degassed	In air	<i>k</i> ₂ / <i>k</i> ₀	Degassed	In air	<i>k</i> ₂ / <i>k</i> ₀
None	4.35	4.39	1.00	4.36	4.32	1.00
0.010	5.30	5.27	1.21	4.40	4.41	1.01
.0272	7.28	7.31	1.67	4.62	4.62	1.06
.0400	7.99	8.01	1.83			
.0450				4.65		1.07
.0454	8.85	8.70	2.00			
.0680				4.74		1.09
.0681	11.9	12.9	2.8			

^a in l./mole sec. ^b For purification procedure see Experimental.

The Effect of Light.—These results make clear the important fact that triethylamine is not a catalyst for the reaction of pure sulfur with pure triphenylphosphine in the dark and does not become so by the mere presence of oxygen. The powerful catalytic effects previously observed must be due to the joint action of the base and of some impurity, presumably present in the sulfur. The field of search for this impurity is narrowed by the observation that it is generated rapidly when the reactant solutions are exposed to light in the presence of air before the run. Thus, a kinetic experiment at

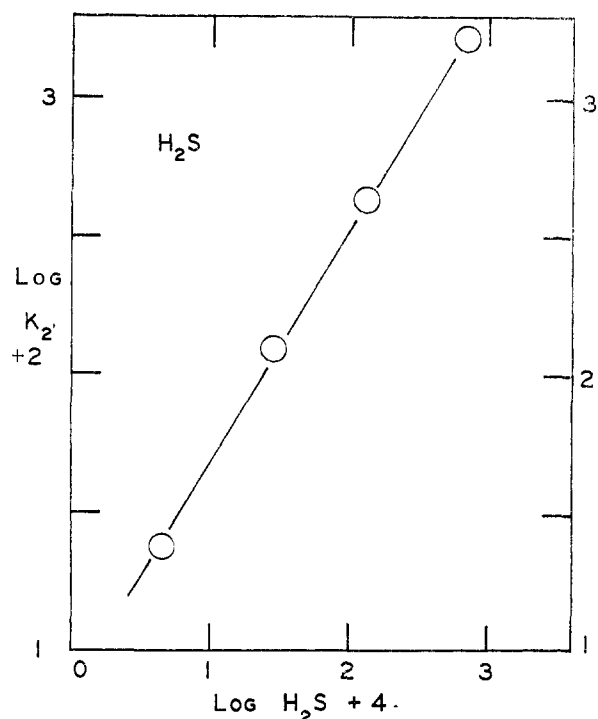


Fig. 4.—Effect of hydrogen sulfide upon reaction of triphenylphosphine with sulfur in benzene at 25°.

an amine concentration of 0.010 *M* gave a second order rate constant of 5.27×10^{-3} without exposure to light; one hour in indoor light under air before mixing led to a rate constant of 15×10^{-3} . At an amine concentration of 0.040 *M*, the corresponding figures were 8.0 and 66×10^{-3} . The important factor is the exposure to light before reaction and not the question of illumination during the period of the rate measurement. It seems likely that the effect of any oxidant produced by triphenylphosphine, as in the aging experiments on the uncatalyzed reaction, will be magnified by the presence of triethylamine in two ways (1) the formation of sulfur dioxide from sulfur may well be made rapid and thus the observed reaction be of the second order and not autocatalytic in form and (2) the presence of triethylamine and water may convert sulfur dioxide to the very thiophilic¹⁰ bisulfite ion, which can take part in the reaction as discussed below.

Sulfur Dioxide and Hydrogen Sulfide with Triethylamine.—In view of these considerations, a series of experiments was conducted to determine the possible role in the amine-catalyzed sulfur-triphenylphosphine reaction of the two most universal impurities in sulfur, namely, sulfur dioxide and hydrogen sulfide. The runs were prepared in total darkness. Both substances proved to be strong co-catalysts, with triethylamine, of the S_8 -triphenylphosphine reaction, but the form of the concentration dependence was quite different in the two cases. For hydrogen sulfide (Table II and Fig. 4) the rate of reaction was directly proportional to the concentration and the results are expressible in the general form

(10) Part II of this series: P. D. Bartlett and R. E. Davis, *This Journal*, 80, 2513 (1958).

$$\frac{d(C_6H_5)_3PS}{dt} = 4.33 \times 10^{-3} (S_8)(C_6H_5)_3P + 1.39 \times 10^4 (S_8)(C_6H_5)_3P(H_2S)(Et_3N)$$

From this result it appears that in the presence of 0.04 *M* triethylamine it would require less than 10^{-6} *M* hydrogen sulfide present in solution to bring about a 10% increase in the rate of formation of triphenylphosphine sulfide. One molecule of H_2S in 25,000 atoms of sulfur would produce a clearly observable effect.

TABLE II

EFFECT OF HYDROGEN SULFIDE ON THE TRIETHYLAMINE-CATALYZED REACTION OF SULFUR WITH TRIPHENYLPHOSPHINE IN BENZENE AT 25° (RUNS PREPARED IN TOTAL DARKNESS, USING RECRYSTALLIZED S_8)

Et_3N, M	$10^4(H_2S)$	10^4k_2	$10^{-4}k_2/(Et_3N)(H_2S)$
0	862	4.50	..
0.0333	0	4.44	..
0	0	4.33	..
0.0333	4.58	220	1.44
.0333	4.58	250	1.64
.0333	28.6	1,220	1.28
.0333	28.6	1,250	1.34
.0333	718	30,000	1.25

TABLE III

EFFECT OF SULFUR DIOXIDE ON THE TRIETHYLAMINE-CATALYZED REACTION OF SULFUR WITH TRIPHENYLPHOSPHINE IN BENZENE AT 25° (CONDITIONS SAME AS IN TABLE II)

$(Et_3N), M$	$(SO_2) \times 10^4, M$	$k_2 \times 10^4$	$k_2^S = k_2 \times 10^4 / -4.52$	$10^{-4}k_2^S/(Et_3N)(SO_2)$
0	0	4.36
0.0239	0 ^a	4.52	0	..
0	130	6.34	1.82	..
0.0239	0.0262 ^a	7.20	2.68	42.6
.0239	0.262	7.13	2.61	4.2
.0239	2.62	19.1	14.6	2.3
.0239	4.28	60.0	55.5	5.4
.0239	4.28 ^a	64.0	59.5	5.8
.0239	26.2	250	245	3.9
.0239	42.8 ^a	460	455	4.5
.0239	42.8	360	355	3.5
.0239	131 ^a	500	495	1.6
.0239	142	430	425	1.25
.0239	142 ^a	470	465	1.4
.0239	142	560	555	1.6
.0239	142	540	535	1.6
.0239	150	580	575	1.6

^a These runs were done without vacuum line technique; in all other runs the vacuum line was used.

The results with sulfur dioxide are shown in Table III and Fig. 5. As previously mentioned, sulfur dioxide alone is a catalyst for the reaction, but its effectiveness is increased about a thousand-fold by the presence of 0.0239 *M* triethylamine, the standard concentration employed in the experiments of Table III. Unlike hydrogen sulfide, sulfur dioxide is not uniformly effective as a catalyst, the relative catalytic power declining with increasing concentration. Since in the experiments quoted the sulfur dioxide was never equivalent to more than 6.3% of the amine present, this declining effectiveness cannot be due to approaching a complete conversion of the amine into salt or complex

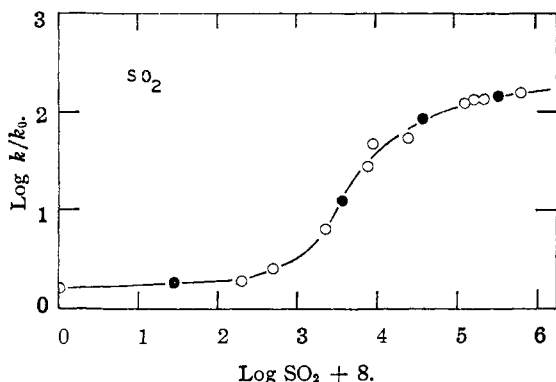


Fig. 5.—Effect of sulfur dioxide upon reaction of triphenylphosphine with sulfur in benzene at 25°.

with the sulfur dioxide. Although the conditions were intended to be anhydrous, the possibility cannot be excluded that small amounts of water are important in the formation of triethylammonium bisulfite, which might be much more thiophilic than the triethylamine-sulfur dioxide complex. No further investigation was made of the effect of water concentration in addition to that of sulfur dioxide.

Mechanism of the H₂S and SO₂ Co-catalysis with Triethylamine.—We have pointed out above that triethylamine undergoes no detectable interaction with pure sulfur in solution at the concentrations used in these experiments. It is quite otherwise with either hydrogen sulfide or sulfur dioxide present. Hydrogen sulfide produces intensely colored solutions of yellow-orange polysulfides (Fig. 6), the equilibrium color being attained within ten seconds, corresponding to an estimated rate constant greater than 100 l./mole sec. The addition of triphenylphosphine causes an equally rapid disappearance of the deep color with formation of triphenylphosphine sulfide. It is evident from these simple experiments that hydrogen sulfide in the presence of the organic base alters the condition of the sulfur to one in which it is highly reactive toward triphenylphosphine. It is also worth noting that in the experiments of Table II the highest H₂S concentration was twice the amine concentration, yet the proportionality of the rate to the former was undisturbed. This is possible only because the acid and basic strengths involved are so low that the concentration of the species Et₃NHSH (as a hydrogen-bonded ion pair) is never more than a small fraction of the total hydrogen sulfide concentration.

Since in aqueous solutions the sulfide and hydro-sulfide ions convert molecular sulfur into polysulfide ions, the deeply colored material in benzene is very probably of this form but existing largely paired with the triethylammonium ion. It is already known (Part I) that noncyclic sulfur chains, as they exist in polymeric sulfur in solution, are very much more reactive toward triphenylphosphine than are S₈ molecules and that a negative charge on a terminal sulfur atom does not prevent the reactivity of triphenylphosphine polysulfides from exceeding that of sulfur in the intermediate steps of the uncatalyzed triphenylphosphine sulfide formation. Thus the mechanism of the co-catalysis by hydrogen

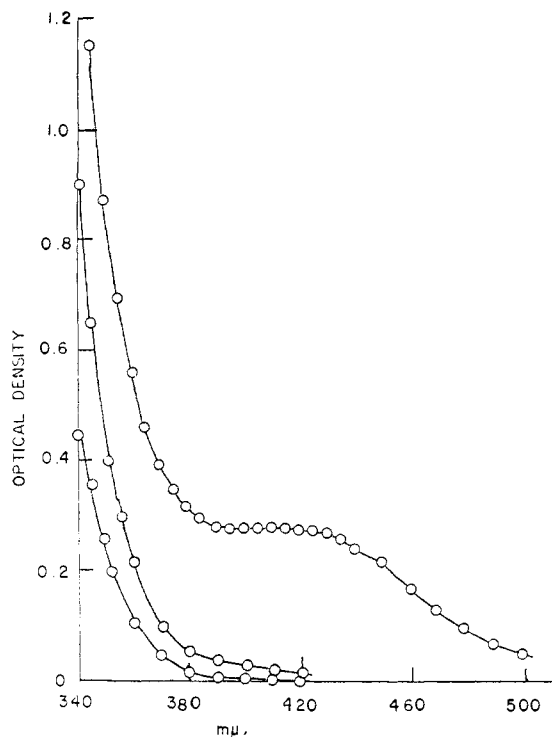


Fig. 6.—Spectra in benzene: lower curve, S₈ ($9.71 \times 10^{-4} M$); middle curve, S₈ ($2.00 \times 10^{-3} M$) + triethylamine ($5.00 \times 10^{-2} M$); upper curve, S₈ ($2.00 \times 10^{-3} M$), triethylamine ($5.00 \times 10^{-2} M$), and hydrogen sulfide ($0.107 M$).

sulfide and triethylamine must be the simple one of converting S₈ into a form in which it resembles reactive S_x.

In the case of sulfur dioxide the situation is less simple because the sulfite ion reacts rapidly with sulfur to produce thiosulfate ion and therefore might be expected to be consumed under the conditions of the co-catalysis. That this actually occurs is indicated by a pair of experiments in the presence of $2.62 \times 10^{-5} M$ sulfur dioxide. When the reactants and catalysts were mixed directly in the usual manner, the second order rate constant was 19.1×10^{-3} . When the amine, sulfur dioxide and sulfur were mixed and allowed to stand 4 hr. before the addition of the triphenylphosphine, the rate constant was 8.4×10^{-3} , suggesting that about half of the sulfur dioxide had been consumed during the incubation period. In all the experiments with sulfur dioxide added, the second order kinetics was not maintained, but the values of the rate constant declined later in each run. The disappearance of sulfur dioxide, however, is very much slower than the catalyzed triphenylphosphine sulfide formation. If, as seems likely, the catalysis is due to the rapid attack of triphenylphosphine on intermediates of the type $-O_3S-S_x^-$, then not every such ion which is produced can lead directly to thiosulfate. This "polythiosulfate" ion, in addition to reacting more vigorously with triphenylphosphine than with bisulfite ion, can probably itself add sulfur to form the ion $-O_3S-S_{x+s}^-$, thus having longer life as a catalytic intermediate than if it were only on its

way to becoming thiosulfate. The fact that the formation of thiosulfate is reversible in acid media¹¹ suggests the possibility that under these mildly basic conditions in benzene the equilibrium may not favor thiosulfate overwhelmingly, and this may help to account for the high catalytic effectiveness of small amounts of sulfur dioxide.

Without an extensive study to determine the reproducibility of the kinetics, a rate measurement was made of the formation of thiosulfate under these conditions. The second order rate constant was 4.18×10^{-2} l./mole sec. at a triethylamine concentration of 0.0409 *M* in the absence of triphenylphosphine.

Any suggestion that this co-catalysis might be due to a salt effect by triethylamine bisulfite, sulfide or even by the triethylamine-sulfur dioxide complex could be ruled out. Acetic acid produces no visible acceleration of the reaction in the presence of excess triethylamine, nor do attainable concentrations of tetra-*n*-butylammonium iodide produce as much as 20% increase in rate.

From the results on the co-catalysis of triphenylphosphine sulfide formation by triethylamine and even traces of hydrogen sulfide and sulfur dioxide, it is now clear why triethylamine alone formerly appeared to be a catalyst, why the rates appeared with any one supply of sulfur to reach a ceiling value with increasing amine concentration and why the magnitude of this catalysis was not the same in the hands of different investigators (with different specimens of sulfur). Without special efforts in the purification of the sulfur, and then the avoidance of those conditions, especially light, which lead to the formation of small amounts of hydrogen sulfide or sulfur dioxide, no sample of sulfur is likely to be found which is free from these co-catalysts.

Estimated Amounts of Impurities in Sulfur.—From the rate measurements of Tables II and III, together with the assumption that triethylamine is noncatalytic toward pure sulfur and triphenylphosphine, we may estimate the content of hydrogen sulfide or sulfur dioxide which would account for the behavior of the several samples of sulfur in Fig. 3 (Table IV). The figures in Table IV

TABLE IV
ESTIMATED CONTAMINATION OF SULFUR SAMPLES OF FIGURE 3, BASED ON THEIR KINETIC BEHAVIOR

Sulfur sample	Contamination (molecules per 1000 atoms sulfur)	
	H ₂ S	SO ₂
Curve 1 (Meguerian)	30	8
Curve 2	3	0.8
Curve 3 ("recrystallized" S ₈)	0.3	.08
Curve 4 ("Bacon-Fanelli" S ₈)	0.02	.006

refer, of course, to the amount of co-catalyst present at the moment of reaction; our experience with dark technique showed that, regardless of the care with which the sulfur is purified, co-catalysts are produced during exposure to light with access of air for brief periods. In making the calculations in Table IV the fourth order rate constant for co-catalysis by sulfur dioxide and tri-ethylamine was

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

taken as 5×10^4 , the largest value observed with any consistency over a range of concentration.

As an impurity in the samples of sulfur represented in Fig. 3, sulfur dioxide seems much more probable than hydrogen sulfide. First, lower concentrations are required to produce the observed effects. Second, the ease with which the rates of reaction are increased on standing in air and light is more consistent with an oxidation process. On the other hand, reasons will be given in Part V for thinking that in the irradiation of sulfur with sunlight in organic solvents hydrogen sulfide is an important by-product.

Thiophenol as a Co-catalyst.—Thiophenol also accelerated the triphenylphosphine sulfide formation in the presence of triethylamine. The thiophenolate ion could be behaving in the same manner as postulated for the ion HS⁻. However, since diphenyldisulfide was found as a product, it is clear that the thiophenol has produced an equivalent amount of hydrogen sulfide, which can itself be a co-catalyst. As reported by Schönberg,^{12,13} diphenyldisulfide was observed to react with triphenylphosphine in the presence of water to yield triphenylphosphine oxide and thiophenol.

The Rate of Uncatalyzed Reaction of Triphenylphosphine with S₈.—It has been observed previously that both light-produced poly-sulfur and hexatomic sulfur, S₆, reacted with triphenylphosphine without catalyst too fast for the rate to be measured. We have now succeeded in measuring the rate of this uncatalyzed reaction at 7.35° in dilute benzene solution (Table V).

TABLE V
UNCATALYZED FORMATION OF TRIPHENYLPHOSPHINE SULFIDE FROM HEXATOMIC SULFUR IN BENZENE AT 7.35°

10 ⁴ (S ₈), <i>M</i>	10 ⁴ (C ₆ H ₆) ₂ P, <i>M</i>	<i>k</i> ₂ , l./mole sec.
2.98	8.87	18.8
5.96	4.44	20.2
5.96	4.44	19.8
6.60	8.00	17.8
10.0	6.00	19.0

Av. 19.1 ± 0.7

From the rate measurements of Part I¹ the activation energy of the uncatalyzed reaction of S₈ with triphenylphosphine was determined to be 16.5 kcal., and this leads to an extrapolated rate constant of 7.54×10^{-4} l./mole sec. at 7.35°. Thus S₆ and S₈ differ by a factor of 25,000 in their reactivity toward triphenylphosphine at that temperature.

Experimental

Triphenylphosphine.—Some was purchased (Eastman white label grade) and some was prepared under nitrogen by the procedure of Dodonow and Medox.¹⁴ The former material was recrystallized at least 3 times and the latter 6-8 times, from 95% ethanol, being dried at 65° under less than 1 mm. pressure over Drierite or phosphorus pentoxide. The melting range of several purified samples was 80.4-81.4° (uncorrected). Titration with moist iodine indicated about 98.5% purity. The melting range and the titers were not altered by sublimation.

Triphenylphosphine oxide was prepared from triphenylphosphine in benzene by adding the calculated amount of iodine in 95% ethanol. The solution was made slightly

(12) A. Schönberg, *Ber.*, **68**, 163-164 (1935).

(13) A. Schönberg and M. Z. Barakat, *J. Chem. Soc.*, 892 (1949).

(14) J. Dodonow and H. Medox, *Ber.*, **61**, 907 (1928).

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 Ismail⁶ 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 mμ 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.

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[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

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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 mμ. 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

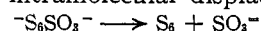
In Part III of this series¹ a preliminary study of the conversion of hexatomic to octatomic sulfur was reported. It was established that this conversion proceeds by way of polymerization of the S₆ followed by depolymerization to S₈. Both stages of the reaction were accelerated by triethylamine. The rates 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.

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

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