

The Acid-Catalyzed Reaction of Triphenylphosphine with Sulfoxides

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Received December 1, 1965

The reaction of triphenylphosphine with sulfoxides produces triphenylphosphine oxide and the corresponding sulfide. The reaction requires acid catalysis, is favored by electron-releasing substituents in the sulfoxide, obeys a Hammett plot with a ρ value of -0.9 , and follows best the first-order rate law. The most likely mechanism of the reaction is a nucleophilic attack by the phosphorus center upon an acid-complexed sulfoxide.

The ability of trivalent phosphorus compounds to abstract an oxygen from N-oxides of tertiary amines,² thioisulfates,³ and acyl peroxides,⁴ suggested that such a reaction should occur also with sulfoxides. While this possibility was being explored, there appeared a short communication by Ray, Shaw, and Smith⁵ on the same subject, but the authors limited themselves to the observation that dimethyl sulfoxide is more reactive than diphenyl sulfoxide. Apparently, these investigators did not extend the reaction to diaryl sulfoxides by means of acid catalysis.

Experimental Section and Results

Materials.—Triphenylphosphine was purchased from Metal Thermite Corp. and crystallized from methanol to a mp 80–80.5° before use. It was free of the corresponding oxide, as shown by infrared spectra and thin layer chromatography. Dimethyl sulfoxide, Matheson Coleman, was distilled under vacuum and the middle cut, bp 40° (1 mm), was employed for the study of the reaction. Glacial acetic acid, Baker's Analyzed reagent, was utilized without purification. All of the aromatic sulfoxides were prepared and purified by procedures described in the literature. The only innovation consisted of the use of dimethyl sulfoxide as an efficient reaction medium for the methylation of di-*p*-hydroxyphenyl sulfoxide.

The mixture of 23.4 g (0.1 mole) of di-*p*-hydroxyphenyl sulfoxide, 8.8 g (0.21 mole) of sodium hydroxide, and 100 ml of dimethyl sulfoxide was stirred at room temperature. The resulting homogeneous solution was cooled to 0° and a cooled portion⁶ of 100 g of methyl bromide (1.05 moles) was added at once. The reaction flask was equipped with a Dry Ice condenser and the mixture was stirred during 18 hr allowing it to come to room temperature. The precipitate of sodium bromide was filtered, and the filtrate was poured into 400 ml of water. The product obtained in 92% yield (20 g) was crystallized from ethanol to give di-*p*-methoxyphenyl sulfoxide, mp 95–96° (lit.⁶ mp 93–94°).

Reaction of Dimethyl Sulfoxide and Triphenylphosphine.—A number of experiments were carried out by heating solutions of triphenylphosphine in dimethyl sulfoxide while a stream of nitrogen was bubbled through the reaction mixture into a 0.2 *M* aqueous solution of mercuric chloride. The precipitate of $[(\text{CH}_3)_2\text{S}]_2 \cdot 3\text{HgCl}_2$ ⁷ was filtered, washed, dried, and identified by its mp 150–151°.

Pure reagents failed to produce an evolution of dimethyl sulfide even when the solution was refluxed during the period of 1 hr (at 189°), while the addition of catalytic amounts of sulfuric acid gave an immediate liberation of dimethyl sulfide. Triphenylphosphine oxide was isolated from the reaction mixture in better than 70% yields. Control experiments consisting of heating dimethyl sulfoxide in the presence of catalytic amounts of sulfuric acid liberated only traces of dimethyl sulfide. At 100° the

control experiment failed to produce visible amounts of the mercuric chloride complex of dimethyl sulfide upon heating for 1 hr, but successive additions of known portions of triphenylphosphine gave quantitative amounts of the complex.

The heating of dimethyl sulfoxide in glacial acetic acid for 2 hr at 100° failed to give any liberation of dimethyl sulfide, but successive additions of known amounts of triphenylphosphine again gave stoichiometric quantities of the mercuric chloride complex of dimethyl sulfide, and triphenylphosphine oxide was isolated from the final reaction mixture by dilution with water.

Reaction of Diaryl Sulfoxides with Triphenylphosphine.—The reaction of diaryl sulfoxides with triphenylphosphine was carried out under an atmosphere of nitrogen in solutions of glacial acetic acid, and in the presence of known amounts of boron trifluoride. The results of a series of definitive experiments with a variety of sulfoxides are summarized in Table I. In most cases the occurrence of the reaction was determined by the isolation of the sulfide derived from the starting material and of triphenylphosphine oxide in the form of the complex with boron trifluoride (*vide infra*).

A series of experiments was carried out with several diaryl sulfoxides to determine the relative progress of the reaction over fixed periods of time as a function of changes in the structure of the sulfoxide and the concentration of the reagents. In all cases the solutions in glacial acetic acid were maintained under reflux in an atmosphere of nitrogen for the indicated period of time. The reaction mixtures were then cooled rapidly in an ice bath and 0.016 mole of boron trifluoride etherate was added in order to precipitate the oxide of triphenylphosphine as the complex with boron trifluoride (*vide infra*). The complex was isolated by filtration in a sintered-glass funnel, dried *in vacuo* to constant weight, and weighed. The results of these experiments are summarized in Table II. The extent of the reaction was determined on the basis of the yield of the oxide of triphenylphosphine.

A Quantitative Method for the Isolation of the Oxide of Triphenylphosphine as the Complex with Boron Trifluoride.—In view of the failures to apply spectroscopic methods for the determination of either the disappearance of the sulfoxides and triphenylphosphine, or the appearance of diaryl sulfide and triphenylphosphine oxide, a method was developed based on the precipitation of the latter as the complex with boron trifluoride.

Aliquots of the reaction mixtures were treated with an excess of boron trifluoride etherate and the complex was allowed to precipitate from the ice-cold mixture. An authentic sample of this complex was prepared from the two components to give white needles⁸ of mp 239–240° which crystallized well from hot acetic acid.

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{OP} \cdot \text{BF}_3$: C, 62.77; H, 4.37. Found (Alfred Bernhardt, M lheim, Germany): C, 62.46; H, 4.37.

In order to improve the quantitative aspects of the isolation of the above mentioned complex, there were prepared two standard solutions of the oxide in 250.00 ml of glacial acetic acid, and known volumes of these solution were diluted to 50.00 ml with glacial acetic acid and treated with 2 ml of boron trifluoride etherate. The resulting precipitates were filtered, dried *in vacuo* to constant weight, and weighed in tared sintered-glass funnels. Table III summarizes the experimental results, and the resulting calibration curve is shown in Figure 1. The best straight line was determined by the least-squares method, and is given by the equation $Y = 0.0712 + 1.00x$. The latter was employed to correct the experimentally determined weights of the complex.

The Kinetics of the Reaction.—The kinetic experiments were carried out in solutions of glacial acetic acid under an atmosphere

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(2) (a) E. H. Howard and W. F. Olszewski, *J. Am. Chem. Soc.*, **81**, 1483 (1959); (b) T. R. Emerson and C. W. Rees, *J. Chem. Soc.*, 1917 (1962).

(3) J. F. Carson and F. O. Wong, *J. Org. Chem.*, **26**, 1467 (1961).

(4) (a) F. Challenger and J. K. Wilson, *J. Chem. Soc.*, 213 (1927);

(b) D. B. Denny and M. Greenbaum, *J. Am. Chem. Soc.*, **79**, 979 (1957).

(5) K. S. Ray, R. A. Shaw, and B. C. Smith, *Nature*, **196**, 372 (1962).

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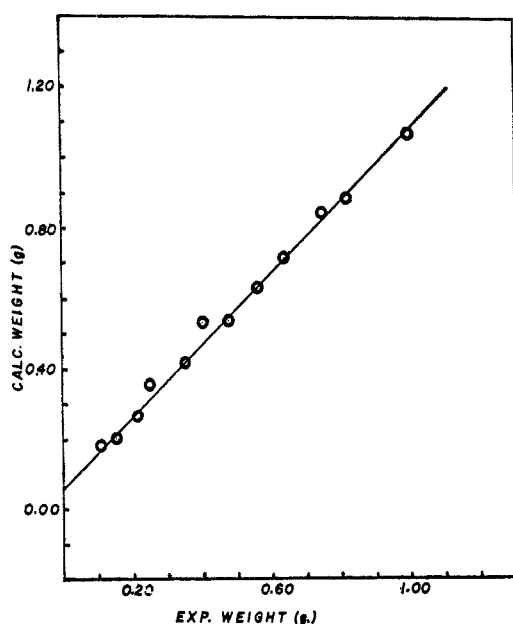
(7) W. F. Faragher, J. C. Morrell, and S. Comay, *J. Am. Chem. Soc.*, **51**, 2781 (1929).

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TABLE I: THE REACTION OF AROMATIC SULFOXIDES WITH TRIPHENYLPHOSPHINE

$-(p\text{-RC}_6\text{H}_4)_2\text{SO}-$ R	Moles $\times 10^2$	Ph ₃ P, moles $\times 10^2$	AcOH, ml	BF ₃ , moles $\times 10^2$	Temp, °C	Time, hr	Ph ₃ POBF ₃ , ^a % yield	Sulfide, ^b % yield
CH ₃	3.0	3.0	50	None	118	4.0	None	None
Br	3.0	3.0	50	None	118	12.0	None	None
CH ₃	20.0	20	100	32	118	2.0	86	68
CH ₃	3.0	3.0	50	16	72	5.0	None	c
CH ₃	3.0	3.0	50	16	118	4.0	80	75
CH ₃	3.0	3.0	50	0.37 ^d	118	4.0	35	c
Br	10.0	10.0	100	32	118	9.0	75	59
Cl	20.0	20.0	100	32	118	5.0	88	24
H	3.0	3.0	50	16	118	1.25	87	66 ^e
NO ₂	3.0	3.0	50	16	118	4.25	None	None
f	3.0	3.0	50	16	118	4.0	95	68

^a An excess of boron trifluoride was added for the purpose of isolation of this complex. ^b The sulfides were identified by melting points and mixture melting points with authentic samples. No special efforts were exerted to ensure complete isolation of the sulfides from the final reaction mixtures diluted with water. ^c No attempt was made to isolate the sulfide in view of the low yield of Ph₃POBF₃. ^d Concentrated sulfuric acid in place of boron trifluoride. ^e This sulfide was isolated by distillation and identified as the corresponding sulfone. ^f Phenoxathiin-10-oxide.

Figure 1.—Calibration curve for the gravimetric analysis of Ph₃PO·BF₃.TABLE II
THE YIELDS OF THE OXIDE OF TRIPHENYLPHOSPHINE IN
THE REACTIONS OF AROMATIC SULFOXIDES
WITH TRIPHENYLPHOSPHINE

$-(p\text{-RC}_6\text{H}_4)_2\text{SO}-$ R	Moles $\times 10^2$	Ph ₃ P, moles $\times 10^2$	BF ₃ , moles $\times 10^2$	Time, hr	% reaction ^a
H	6.0	6.0	8.0	1	64
H	6.0	6.0	16.0	1	89
H	6.0	6.0	8.0	2	85, 86
CH ₃	6.0	6.0	8.0	1	82, 82
CH ₃ O	6.0	6.0	8.0	1	79
Cl	6.0	6.0	8.0	1	28
Cl	6.0	6.0	16.0	1	54, 55, 57
Br	6.0	6.0	8.0	2	43, 46, 46
Br	6.0	6.0	16.0	2	70, 71
Br	6.0	6.0	24.0	2	83, 85
Br	6.0	6.0	32.0	2	88, 92
Br	6.0	6.0	40.0	2	100
Br	9.0	6.0	8.0	2	83
Br	12.0	6.0	8.0	2	96
Br	6.0	9.0	8.0	2	55
Br	6.0	12.0	8.0	2	55

^a In glacial acetic acid at reflux temperature. The yields of Ph₃POBF₃ were corrected as described elsewhere in this paper.

TABLE III
THE QUANTITATIVE ASPECTS OF THE ISOLATION OF
THE BORON TRIFLUORIDE COMPLEX OF
TRIPHENYLPHOSPHINE OXIDE

Aliquot, ml	Weight of complex, g	
	Calcd	Found
5.00 ^a	0.0882	0.0000
5.00 ^b	0.1038	0.0000
10.00 ^a	0.1764	0.1140, 0.1076
10.00 ^b	0.2077	0.1483
15.00 ^a	0.2647	0.2054
20.00 ^a	0.3529	0.2481, 0.2927
20.00 ^b	0.4153	0.3391
30.00 ^a	0.5293	0.4781
30.00 ^b	0.6230	0.5593
40.00 ^a	0.7057	0.6486
40.00 ^b	0.8306	0.7472
50.00 ^a	0.8820	0.8284
50.00 ^b	1.0383	0.9952

^{a, b} The standard solutions were 0.013 and 0.015 M, respectively, in triphenylphosphine oxide dissolved in glacial acetic acid.

of nitrogen. The solutions were placed in a constant-temperature bath maintained at $116 \pm 0.1^\circ$, and at zero time, the solution of boron trifluoride in acetic acid was introduced. At room temperature the total volume of the solutions was 250 ml, and since aliquots of 50 ml were being removed at 116° , a correction was determined for the expansion of glacial acetic acid on the basis of the weight of a 50-ml volume brought to reflux. The aliquots were rapidly cooled in an ice bath, and the weight of triphenylphosphine oxide was then determined, as described above. The results of representative kinetic experiments are shown in Table IV.

Discussion

It is of interest to note that the reaction of triphenylphosphine occurs with dimethyl sulfoxide in a medium of glacial acetic acid while the aromatic sulfoxides failed to react under these conditions. Since this work definitely shows that the reaction under study is catalyzed by acid, the above difference can be explained on the basis of the greater basicity of dimethyl sulfoxide. If the ability of sulfoxides to participate in hydrogen bonding is a reflection of their relative basicities, then we can cite the fact that, under equivalent conditions, the association constants of dimethyl and diphenyl sulfoxides with phenol are 55 and 19 moles/l., respectively.⁹ This difference in the behavior of the

(9) R. Figueroa, E. Roig, and H. H. Szmant, *Spectrochim. Acta*, in press.

TABLE IV
THE KINETICS OF THE REACTION OF DIARYL SULFOXIDES WITH TRIPHENYLPHOSPHINE IN GLACIAL ACETIC ACID AT 116°

R	(<i>p</i> -RC ₆ H ₄) ₂ SO Moles/l. × 10 ²	Ph ₃ P, moles/l. × 10 ²	BF ₃ , moles/l. × 10 ²	Time, hr	% reaction	<i>k</i> , hr ⁻¹				
H	6.0	6.0	6.0	0.75	29	0.41				
				1.25	43	0.45				
				1.75	59	0.51				
				2.00	67	0.59				
				2.50	78	0.59				
						Av 0.51 ± 0.07 0.44 ± 0.04 ^a				
H	6.0	6.0	8.0	1.0	49	0.67				
				2.0	85	0.93				
						Av 0.80 ± 0.17				
H	6.0	6.0	9.4	0.75	44	0.80				
				1.25	65	0.84				
				1.50	71	0.82				
				1.75	76	0.80				
				2.00	79	0.70				
						Av 0.81 ± 0.02				
H	6.0	6.0	11.6	0.17	13	0.88				
				0.33	28	0.97				
				0.50	44	1.2				
				0.75	63	1.3				
				1.00	72	1.3				
						Av 1.15 ± 0.15 1.11 ± 0.2 ^a				
H	9.0	6.0	8.0	0.50	54	0.89				
				0.75	71	0.85				
				1.00	83	0.80				
				1.25	96	0.83				
				1.67	100					
						Av 0.85 ± 0.05				
H	12.0	6.0	8.0	0.27	20	0.40				
				0.42	41	0.54				
				0.60	68	0.69				
				0.75	85	0.73				
				1.0	98	0.67				
						Av 0.61 ± 0.11				
H	6.0	9.0	8.0	1.0	30	0.39				
				2.0	60	0.46				
				3.0	85	0.63				
										Av 0.51 ± 0.12
H	6.0	12.0	8.0	1.00	18	0.20				
				2.00	39	0.26				
				3.10	67	0.36				
				4.00	74	0.33				
				5.00	87	0.78				
										Av 0.31 ± 0.06 0.26 ± 0.02 ^a
CH ₃	6.0	6.0	8.0	0.25	21	(0.98)				
				0.50	62	2.3				
				0.75	86	2.7				
				1.00	94	2.9				
				1.00	94	2.9				
				1.25	100	2.8				
						Av 2.6 ± 0.3				
Br	6.0	6.0	8.0	1.00	35	0.42				
				2.00	55	0.40				
				3.00	72	0.42				
				3.50	79	0.42				
				4.00	84	0.47				
						Av 0.43 ± 0.02				

^a Duplicate experiments.

aliphatic and aromatic sulfoxides also implies that the acid catalysis involves the sulfoxides rather than the phosphine. The dependence of the reaction on the basicity of the sulfoxide also explains why no reaction was observed in the case of di-*p*-nitrophenyl sulfoxide

under the conditions of the experiments listed in Table I. The association constant of this sulfoxide with phenol is only about one-tenth of that of diphenyl sulfoxide,⁹ and the boron trifluoride employed in the present work is also capable of complexing with the

nitro substituents and this, in turn, is expected to reduce the basicity of the sulfoxide function even further.

In the case of the diaryl sulfoxides it was also possible to use catalytic amounts of sulfuric acid, but in order to avoid complications due to sulfonation, etc., most of the experiments were carried out using boron trifluoride catalysis. This acid, however, forms a strong complex with triphenylphosphine oxide, and consequently it is necessary to employ equimolar quantities.

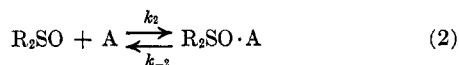
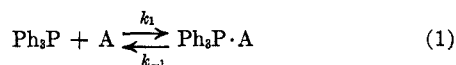
The results of Table II reveal a number of interesting features of this reaction. First of all, under equivalent conditions, the extent of reaction decreases as electron-withdrawing substituents are introduced. The only exception to this trend is the behavior of the *p,p'*-dimethoxy-substituted sulfoxide, and here again, as in the case of the nitro group, the reason must lie with the fact that we are dealing with substituents complexed with boron trifluoride.

Secondly, the results of Table II establish without any doubt the dependence of the extent of reaction on the concentration of boron trifluoride. For reasons discussed below it may be suspected that this dependence increases inversely with the basicity of the sulfoxide. This point is emphasized by the larger increase of the extent of the reaction caused by the doubling of the boron trifluoride concentration in the case of the chloro- and bromo-substituted sulfoxides when compared to the parent compound.

Finally, the series of experiments with di-*p*-bromophenyl sulfoxide indicates that the reaction is also strongly favored by an increase in the initial concentration of the sulfoxide, but not so by an increase in the initial concentration of the phosphine.

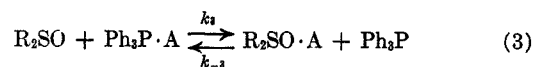
All of these results, as well as the fact that, in spite of the limitations of the kinetic measurements, the reaction seems to follow best the first-order rate law (see Table IV), are compatible with the following mechanism.

It stands to reason that the basic reagents, triphenylphosphine and the sulfoxide, participate in the interlocking equilibria, shown in eq 1 and 2 where A repre-

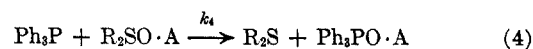


sents boron trifluoride or a proton. We ignore, for the sake of simplicity, the interaction of A with solvent molecules.

We can combine the above equilibrium expressions to give



Now, we can assume the rate-determining step to be the nucleophilic attack of the triphenylphosphine upon the acid-complexed sulfoxide



and, in view of the greater affinity of the triphenylphosphine for the acid catalyst, we apply a steady-state condition to the acid-complexed sulfoxide.

$$\frac{d[\text{R}_2\text{SO}\cdot\text{A}]}{dt} = 0 = k_3[\text{R}_2\text{SO}][\text{Ph}_3\text{P}\cdot\text{A}] - k_{-3}[\text{R}_2\text{SO}\cdot\text{A}][\text{Ph}_3\text{P}] - k_4[\text{R}_2\text{SO}\cdot\text{A}][\text{Ph}_3\text{P}]$$

Thus

$$[\text{R}_2\text{SO}\cdot\text{A}] = \frac{k_3[\text{R}_2\text{SO}][\text{Ph}_3\text{P}\cdot\text{A}]}{k_{-3}[\text{Ph}_3\text{P}] + k_4[\text{Ph}_3\text{P}]}$$

and

$$\text{rate} = k_4[\text{Ph}_3\text{P}][\text{R}_2\text{SO}\cdot\text{A}] = \left(\frac{k_3 k_4}{k_{-3} + k_4} \right) [\text{R}_2\text{SO}][\text{Ph}_3\text{P}\cdot\text{A}] \quad (5)$$

We can assume that during the initial phase of the reaction the concentration of $[\text{Ph}_3\text{P}\cdot\text{A}]$ remains essentially constant because equilibrium (1) tends to replenish the phosphine which is being consumed, and this then can be the reason why the reaction is seen to follow a pseudo-first-order rate law.

The conclusion that the acid catalysis involves the sulfoxide rather than the phosphine moiety is supported by the observation that acetic acid catalyzes the reaction of only the most basic⁹ of all the sulfoxides investigated so far, namely, dimethyl sulfoxide. The latter fails to react with triphenylphosphine in a neutral medium such as benzene, and its reaction in carbon tetrachloride¹⁰ is attributed to the formation of an active species from an initial reaction between triphenylphosphine and carbon tetrachloride. The dependence of the reactivity of the sulfoxide upon its relative basicity is also supported by the linear Hammett relationship which is obtained when the rate constants of the *p*-methyl-, *p*-bromo-, and the unsubstituted phenyl sulfoxide are plotted *vs.* the normal σ values. Unfortunately, the *p*-methoxy-substituted compound cannot be included in this treatment for reasons explained above, but on the basis of three experimental points one can estimate a ρ value of -0.9 . This value compares favorably with the ρ of -0.65 obtained⁹ for the association of sulfoxides with phenol in carbon tetrachloride.

(10) J. Castrillón and H. H. Szmant, *J. Org. Chem.*, **30**, 1338 (1965).