Discussion of Results

The equilibrium constant is dependent upon the nth power of the hydrogen ion concentration. It was assumed that the metal chelate compound was PrT_3. Rewriting the equilibrium expression in logarithmic form gives

$$\log K_{eq} = \log \text{D.R.} + n \log [H^+] - 3 \log [HT]$$

or

$$\log \text{D.R.} = -n \log [H^+] + 3 \log [HT] + \log K_{eq}$$

A plot of log D.R. *vs.* $-\log[H^+]$ should give a straight line whose slope, n, is both the average charge on the aqueous praseodymium species and the exponent for evaluating H^+ in the equilibrium expression.

The data were plotted (see Fig. 1) and the slope of the line was calculated by the method of least squares, yielding values of 2.96 for the 0.2 *f* and 2.93 for the 0.5 *f* TTA. Since these values are within experimental error of the limiting value, 3, K_{eq} was calculated assuming that $n = 3$. These results are given in Table I. The D.R. values shown in the same table have already been corrected for the activity coefficient of the species involved. No correction for the solubility of TTA in water (2%) was made.

The values marked with an asterisk (*) indicate that this result was approached from the benzene phase. In these runs, all of the praseodymium ions were initially extracted into the benzene phase at a high *p*H, *ca.* 4.4–4.5. Following this, the phases were separated and the aqueous phase discarded. A solution containing the proper amount of ammonium chloride was added to the reaction vessel and the contents were again allowed to approach equilibrium. The results of these runs agree with those obtained by introduction of the praseodymium chloride in the aqueous phase.

TABLE I

0.2 *f* TTA			0.5 *f* TTA		
*p*H	D.R.	$K_{eq} \times 10^9$	*p*H	D.R.	$K_{eq} \times 10^9$
3.00	0.0183	3.3	2.85	0.0934	3.8
3.10	.0406	3.8	2.90	.139	4.0
3.20	.0771	3.4	3.00	.226	3.9
3.25	.100	3.2	3.10	.464	3.4
3.30	.204	4.6	3.18	.720	3.1
3.34	.235	4.0	3.20	.856	3.1
3.35	.259	3.8	3.30	1.34	2.5
3.46	.436	3.2	3.38	2.79	3.0
3.50	.529	3.0	3.41	3.11	2.7
3.60	1.01	2.8	3.46*	5.71	3.5
3.69*	2.04	3.3	3.55	11.5	3.7
3.71	2.48	3.3	3.59	19.8	4.9
3.80	5.37	3.8	3.68	23.3	3.1
3.86	6.46	3.0	3.89	96.1	3.0
3.90	6.70	3.4	3.92	134	3.4
3.96*	13.2	3.1		Average	3.4 ± 0.5
4.09*	36.6	3.5			
4.18	61.1	3.1			
4.21	72.9	3.0			
	Average	3.3 ± 0.5			

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The Kinetics of the Oxidation of Phenyl Sulfoxide[1]

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RECEIVED DECEMBER 11, 1953

The comprehensive study of the reactions of ketones with peracids[2] and the recent publications of Overberger and Cummins[3,4] concerning the kinetics of the oxidation of *p*-chlorobenzyl sulfide, make it desirable to record the results obtained in the investigation of the kinetics of the peracid oxidation of phenyl sulfoxide. We wish to publish these results at this time since this work has been temporarily discontinued.

Experimental

The experimental work consists of two groups of experiments. The first group of kinetic experiments was carried out using perbenzoic acid in an acetone medium. The perbenzoic acid (PBA) was prepared according to Swern, *et al.*,[5] by the photochemical oxidation of benzaldehyde in an acetone solution. Phenyl sulfoxide purified by crystallization from methanol (m.p. 70–71°),[6] was dissolved in 80–90 ml. of acetone in a volumetric flask and on addition of PBA the resulting solution was diluted with additional acetone to the 100 ml. mark. The flask was placed in a constant temperature bath at 30.4°, and at desired intervals aliquots were removed and titrated iodometrically.[7] The strength of the PBA stock solution was determined before each experiment. The rate of decomposition of PBA in acetone under identical conditions with those employed in the kinetic runs (except for the absence of the sulfoxide) was found to be insignificant when compored with the reaction rates of the sulfoxide oxidation. Thus, it was found that in a two-hour period less than 10% of the PBA was lost, and the same period of time was sufficient for the completion of about 80% of the sulfoxide oxidation.

The second group of experiments involved the oxidation of the phenyl sulfoxide with peracetic acid (PAA) in a glacial acetic acid medium. Stabilized 40% peracetic acid (Buffalo Electro-Chemical Co.)[8] was diluted with glacial acetic acid and the resulting stock solution was kept in a refrigerator at −5°. This series of kinetic runs was carried out at 29.0° and the reaction rate was followed by iodometric titration of aliquots. The PAA solution contains according to the manufacturer's specifications a minimum of 40% PAA and approximately 5% hydrogen peroxide. In order to determine the total residual active oxygen, an ammonium molybdate-catalyzed iodometric titration was employed.[9]

The experimental results are summarized in Tables I and II. The bimolecular rate law, first order with respect to sulfoxide and to the peracid, was assumed to calculate the rate constant since a linear relationship was obtained when the log $(C_{\text{peracid}})/(C_{\text{PH}_2\text{SO}})$ was plotted against time.

Discussion

Overberger and Cummins[3] concluded that the perbenzoic acid (PBA) oxidation of a sulfide involves a nucleophilic attack of the sulfur atom upon

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[1] From the M.S. thesis of F. K., Duquesne University, August, 1950. Presented in part at the 118th Meeting of the Am. Chem. Soc., 1950.

[2] S. L. Friess and P. E. Frankenburg, THIS JOURNAL, **74**, 2679 (1952), and earlier papers.

[3] C. G. Overberger and R. W. Cummins, *ibid.*, **75**, 4250 (1953).

[4] C. G. Overberger and R. W. Cummins, *ibid.*, **75**, 4783 (1953).

[5] D. Swern, T. W. Findley and J. T. Scanlan, *ibid.*, **66**, 1925 (1944).

[6] W. J. Hickenbottom, "Reactions of Organic Compounds," Longmans, Green and Co., New York, N. Y., 1948.

[7] A. Baeyer and V. Villiger, *Ber.*, **33**, 2481 (1900).

[8] We gratefully acknowledge the gift from the Buffalo Electrochemical Co. for the stabilized peracetic acid which was used in this study. We also wish to thank Dr. Greenspan for his interest in this work.

[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947.

TABLE I

OXIDATION OF PHENYL SULFOXIDE WITH PERBENZOIC ACID AT 30.4°

Initial concentrations of reactants (mmoles) PBA	Ph_2SO	BA[a]	$k \times 10^3$, l. mole^{-1} sec.$^{-1}$
1.835[b]	1.300	...	5.3 ± 0.8
1.835[b]	1.240	...	5.8 ± .8
1.220[b]	1.239	...	4.2 ± .2
1.220[b]	0.783	...	6.4 ± .5
1.220[b]	0.890	...	5.4 ± .5
2.086[c]	1.367	10.00	5.2 ± .6
1.517[c]	0.918	7.54	5.0 ± .6
1.490[c]	.910	7.55	4.9 ± .3
1.490[c]	.810	7.55	4.5 ± .4

[a] The benzoic acid (BA) content was estimated by assuming the original molar quantity of benzaldehyde to have been completely converted to either BA or PBA. [b] First batch of PBA solution. [c] Second batch of PBA solution.

TABLE II

OXIDATION OF PHENYL SULFOXIDE WITH PERACETIC ACID AT 29.0°

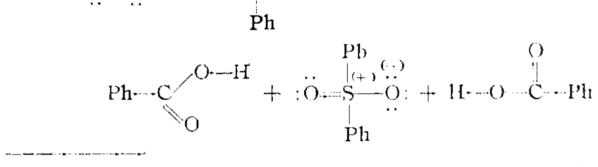
	Initial amounts of reactants (mmoles)			
PAA	Pb_2SO	H_2SO_4[a]	BA	$k \times 10^3$, l. mole^{-1} sec.$^{-1}$
1.474	0.995	0.1160	...	1.57 ± 0.10[d]
1.342	.744	.1058	...	1.36 ± .12[e]
1.342	.842	.1058	...	1.22 ± .08[f]
1.110	.802	.0866	...	0.90 ± .06
1.110	.805	.8066[b]	...	.87 ± .04
1.110	.802	1.6866[b]	...	.81 ± .05
1.110	.802	3.3266[b]	...	.78 ± .02
1.110	.802	6.5666[b]	...	.76 ± .04
1.110	.802	0.0866	0.560	[c]
1.110	.802	.0866	3.810	[c]
1.110	.802	.5666[b]	3.810	[c]
1.110	.802	.0866	0.328	[c]

[a] The commercial PAA contains according to the specifications approximately 1% sulfuric acid. A *p*H titration was carried out in order to determine the sulfuric acid content in the PAA stock solution and was found that each ml. contained 0.0465 mmole of sulfuric acid. [b] Additional sulfuric acid was introduced in the form of a solution of 100% sulfuric acid in glacial acetic acid. [c] Assuming the second-order rate law the rate constants in these experiments varied considerably during the course of the kinetic run. In all cases the relatively high initial values of *k* (approx. 8×10^{-3}) decreased rapidly over the first 50% of reaction and then showed a tendency to approach the constant values of 1.63, 1.67, 2.48 and 2.04 ($\times 10^{-3}$), respectively. [d] At 32.0°. [e] At 31.1°. [f] At 30.0°.

the internally hydrogen-bonded PBA. This conclusion is in accord with the strong nucleophilic character of the sulfur atom of sulfides exemplified in the formation of sulfonium ions, etc.), and it also explains why the oxidation of the sulfide by PBA was not acid catalyzed. The work of Friess and Soloway[10] dealing with the reaction of peracids with ketones has shown that the reactions are acid catalyzed and, furthermore, that the reaction rates obey the first- or second-order rate laws depending on the electron availability at the carbon atom of the carbonyl group of the ketone. Thus, when the electron availability becomes low (because of the presence of electron-withdrawing substituents) then the reaction depended solely on the concentration of the peracid and in extreme cases (*p*-nitro-substituted ketones) the reaction failed to take place. The role of the acid catalyst in the reaction of ketones with peracids is a dual one. It plays a major role in the reactions which follow second-order kinetics and here the acid aids in the polarization of the carbonyl group as is the case in most addition reactions of aldehydes and ketones. When, however, the addition to the carbonyl group becomes difficult because of the presence of electron-withdrawing substituents, then the acid catalyst plays a minor role and the rate-determining step becomes the formation of a powerful oxidizing agent (hydroxylonium ion or oxygen atom) from the decomposition of the peracid.

Let us now examine the results obtained in this study in the light of the conclusions drawn from the studies of peracid reactions with ketones and sulfides. The sulfur atom in sulfoxides is obviously less nucleophilic than the sulfur atom of sulfides, and the situation in the oxidation of sulfoxides by peracids is more closely related to that of the ketones than that of the sulfides. Thus, it is not surprising that the results summarized in Table I show that the oxidation of phenyl sulfoxide by PBA in acetone follows second-order kinetics and that it is subject to catalysis by benzoic acid. It is noted that the rate constant showed rather large variation when the first batch of PBA was employed. This batch was relatively concentrated with respect to PBA and the titer decreased to approximately one-third of its original value with aging. For this reason larger volumes of the PBA solution had to be used and thus larger concentrations of benzoic acid were introduced. The second batch of PBA was less concentrated and the change in titer with time was small, and consequently the benzoic acid concentration was relatively constant. Noteworthy are the rate constants obtained in the experiments (Table I) in which the PBA concentration was kept constant (the titer of PBA solution was constant also) while there was varied the concentration of phenyl sulfoxide. It is noted that the rate constants were inversely proportional to the sulfoxide concentrations or, in other words, directly proportional to the ratios of the benzoic acid/phenyl sulfoxide concentrations.

The most likely mechanism of the oxidation of phenyl sulfoxide by PBA consists of a nucleophilic attack of the PBA on the sulfur atom of the sulfoxide, and the complexing of the latter with benzoic acid would be expected to facilitate such nucleophilic attack.[11]



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[10] S. L. Friess and A. H. Soloway, THIS JOURNAL, **73**, 3968 (1951).

[11] Other reactions which occur most likely *via* a nucleophilic attack upon the sulfur atom of sulfoxides include the formation of sulfonium salts by means of Grignard reagents [Wildi, Taylor and Potratz, THIS JOURNAL, **73**, 1965 (1951)], the formation of sulfoximines by means of hydrazoic acid [Misani, Fair and Reiner, *ibid.*, **73**, 459 (1951)], and the formation of sulfilimines by means of sulfonamides [Tarbell and Weaver, *ibid.*, **63**, 2939 (1941)].

The second group of experiments is summarized in Table II and it employed peracetic acid (PAA) in a medium of glacial acetic acid.[12] It is noted in the first place that the bimolecular rate constants were three to four times smaller than those obtained in the PBA oxidations. This difference can be explained in several ways.

Firstly, Overberger and Cummins[3] have shown that the oxidative strength of peracids increases with the electron-withdrawing character of the group attached to the percarboxy group, and of the phenyl and the methyl groups the former is recognized to be more electron-withdrawing. Secondly, it can be safely assumed that the sulfoxide is more strongly solvated in acetic acid than in acetone, and the higher degree of solvation would tend to inhibit to some degree the successful collisions with the peracid. Overberger and Cummins[4] and Friess[13] similarly explained the decelerating effect of water on the oxidation reactions of sulfoxides and ketones, respectively. Thirdly, the PAA oxidations were carried out in the presence of small amounts of sulfuric acid and the latter was shown to be a negative catalyst. The inhibiting effect of sulfuric acid is worthy of further consideration. It is noted that the magnitude of the effect of sulfuric acid is not very great and that it seems to approach a constant value when the concentration of sulfuric acid exceeds that of phenyl sulfoxide. We attribute the effect of sulfuric acid to the salt formation with the sulfoxide, and the close association of the two ions, or the strong solvation of the sulfoxidonium ion[14] by acetic acid explains the observed decrease in the rate constant. If the sulfuric acid were involved in the formation of a complex with PAA then one would expect a positive catalytic effect.[4] Rather surprising results were obtained when benzoic acid was added to the PAA oxidation experiments (Table II). The rate constants calculated on the basis of a bimolecular rate law were very large during the initial period, then decreased rapidly, and at approximately 50% reaction they approached a constant value. It is difficult to suggest a clear cut explanation of these results because of the complexity of the reaction mixture. However, it seems reasonable to assume an equilibrium between PAA and benzoic acid, and the simultaneous oxidation of phenyl sulfoxide by PAA and PBA. Since the initial values of the oxidation rates were higher than those obtained when PBA in acetone was employed, it is possible that under these conditions there is also made a contribution by a sulfuric acid-catalyzed PBA oxidation. The latter would have a better chance in the polar medium of acetic acid than in the medium of acetone.

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(12) The kinetics of the oxidation of phenyl sulfoxide by PAA was previously investigated by J. Böeseken and E. Arrias [*Rec. trav. chim.*, **54**, 711 (1935)]. These investigators also found the reaction to obey the bimolecular rate law but their rate constant varied considerably from one experiment to another. Thus, in two experiments at 24° they obtained rate constants of 7.2 and 4.45 ($\times 10^{-3}$) and variations such as these were attributed to the spontaneous decomposition of PAA since the rate constants seemed to increase as higher concentrations of PAA were employed. These difficulties are largely avoided in this study since the PAA employed here contained a stabilizer which makes spontaneous decomposition negligible over the period of two hours.

(13) S. L. Friess, THIS JOURNAL, **71**, 2571 (1949).

(14) H. H. Szmant and G. A. Brost, *ibid.*, **73**, 4175 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Ferrocene Derivatives. Part I. The Direct Synthesis of Substituted Ferrocenes

BY P. L. PAUSON[1]

RECEIVED SEPTEMBER 14, 1953

A series of phenyl-substituted ferrocenes is prepared from the corresponding phenyl-substituted cyclopentadienes. Use of a mixture of cyclopentadiene and phenylcyclopentadiene affords the monophenylferrocene. The preparation of 1,1′-dibenzhydrylferrocene from benzhydrylcyclopentadiene provides direct proof that both rings are substituted in the diacylation of ferrocene. Phenylcyclopentadiene and 1,2,3-triphenylcyclopentadiene have been obtained for the first time.

The discovery that the reaction of cyclopentadienylmagnesium bromide with ferric chloride results in the formation of ferrocene (biscyclopentadienyliron(II)),[2] was followed by the demonstration[3] that a variety of both mono- and disubstituted derivatives can be prepared from this compound by acylation under Friedel–Crafts conditions. This method, however, has obvious limitations; to obtain aryl-substituted derivatives in particular, other methods are necessary. After an unsuccessful attempt to introduce phenyl groups into ferrocene by reaction with benzoyl peroxide, it was decided to examine the possibility of preparing the desired products directly from suitably substituted cyclopentadienes.

The preparation of dibenzoferrocene (bis-indenyliron(II)) from indenyllithium has recently been described,[4] but no other application of this reaction to a substituted cyclopentadiene has been reported. It is now shown that derivatives of ferrocene substituted by aryl or alkyl groups in both rings may be obtained readily in this way. Moreover, one example is given to show that monosubstituted derivatives likewise can be obtained if a mixture of the appropriately substituted cyclopentadiene with unsubstituted cyclopentadiene is used in the Grignard reaction.

Of the seven possible cyclopentadienes bearing phenyl substituents (excluding isomers with two

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(1) Chemistry Department, The University, Sheffield 10, England.

(2) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(3) R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

(4) P. L. Pauson and G. Wilkinson, *ibid.*, **75**, 2024 (1953).