

Studies on the Reaction between Peroxydisulfate Ions and Aromatic Amines. The Boyland-Sims Oxidation

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Abstract: Aromatic amines and persulfate ions react in aqueous base to give a 45–55% yield of *o*-aminoaryl sulfate, ammonia, and a polymeric material known as humic acid. The reaction is first order in neutral amine and initially first order in persulfate ion. The effect of substituents on the rate of the reaction, the activation parameters, and the lack of effect of a radical trap suggest a nucleophilic displacement by the amine nitrogen on peroxide oxygen to give the corresponding arylhydroxylamine O-sulfonate. This postulated intermediate may then rearrange to the *o*-aminoaryl sulfate or be oxidized by persulfate to humic acid and ammonia.

The reaction between aromatic amines and peroxydisulfate (persulfate, peroxydisulfate) ions in aqueous base to form *o*-aminoaryl sulfates was first reported in 1953.¹ The preparative aspects of this reaction were explored in a series of further papers which established the scope of the reaction.^{2–4} The reaction might appropriately be named the Boyland-Sims oxidation. Primary, secondary, and tertiary aromatic amines are all successfully converted to the *o*-sulfate esters, although the yields of isolated material are frequently poor. The range is generally between 10 and 40%. If both *ortho* positions are blocked, *para* substitution takes place. Otherwise, *ortho* substitution is exclusive except for the case of the persulfate oxidation of anthranilic acid⁵ in which a small proportion of the *para* isomer was detected. Much starting material is generally recoverable, even though an excess of persulfate is used. The reaction mixtures are highly colored^{2,6} and a number of products in addition to the sulfate esters have been reported. Azo and azoxy compounds have been isolated⁴ and a substituted quinone imine has been found as a product of the oxidation of 2-naphthylamine.¹ The formation of insoluble, brown, amorphous material, frequently in substantial amounts, has been noted in a number of these oxidations.^{1,3,4} The scope of the reaction has been extended to include indoles and aminopyrimidines.^{7,8} The results of a preliminary mechanistic study of this reaction⁹ suggested that it proceeds *via* a nucleophilic displacement on peroxide oxygen¹⁰ rather than by a radical mechanism, and that it is, therefore, closely allied to the Elbs persulfate oxidation of phenols¹¹ with the notable exception of the orientation of the sulfate group. This investigation was undertaken with the hope of defining those

differences between the phenol and the amine oxidations which for the latter case lead to preferential *ortho* substitution.

Materials and Methods

2-Amino-3-hydroxypyridine and 2-amino-3-pyridyl hydrogen sulfate were prepared by the persulfate oxidation of 2-aminopyridine according to Boyland and Sims.⁴ 2,2'-Azopyridine and 2-nitropyridine were prepared according to Kirpal and Böhm.¹² 2-Amino-3,5-dideuteriopyridine was prepared by heating 20 g of D₂O, 4.7 g of 2-aminopyridine, and 2.45 g of sulfuric acid in a sealed tube at 180° (refluxing 2-octanol) for 90 hr. At the end of this period, the tube was cooled, the contents removed, and the volatile material removed *in vacuo*. An additional 20 g of D₂O was then added and the heating repeated. A third run was then completed following which the reaction mixture was made basic with sodium hydroxide and extracted continuously with ether. The ether was removed and the material crystallized from *n*-hexane-ether. The yield was 2.7 g. The calculated isotopic purity is 99.8%. Examination of the nmr spectrum of the product in D₂O showed no trace of the multiplet attributable to the 3 and 5 protons centered at τ 3.4, and the collapse of the 4-proton triplet to a singlet at τ 2.4. Other amines were obtained from Eastman or Aldrich and were either redistilled or recrystallized before use. Inorganic compounds were reagent grade and were used without further purification.

Kinetic runs were carried out in a water bath held to within 0.1° of the indicated temperature. The kinetics of the reactions were followed by measurement of persulfate concentration as a function of time using the iodometric method of Kolthoff and Carr¹³ with the modification that the reaction aliquots were quenched in acetic acid which was consequently present during the 15-min incubation. The blank value was 0.1 ml of 0.01 *M* thiosulfate. Kinetics were run under pseudo-first-order conditions with the amine present in at least tenfold excess. The formation of 2-amino-3-hydroxypyridine was followed by assay with the Folin phenol reagent, essentially according to the method already described.¹¹ Hydrolysis of the sulfate ester was complete within 5 min at 100° in 3 *N* HCl. The blue color produced by the reduction of the Folin phenol reagent

- (1) E. Boyland, D. Manson, and P. Sims, *J. Chem. Soc.*, 3623 (1953).
- (2) E. Boyland and P. Sims, *ibid.*, 980 (1954).
- (3) P. Sims, *ibid.*, 44 (1958).
- (4) E. Boyland and P. Sims, *ibid.*, 4198 (1958).
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- (13) I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, **25**, 298 (1953).

was measured in a Klett-Summerson photoelectric colorimeter using the 660-m μ filter. 2-Aminopyridine does not interfere. 2-Amino-3-hydroxypyridine (0.1 μ mole) gave a Klett reading of 90. Beer's law was obeyed up to at least a Klett reading of 400. 2-Amino-3-hydroxypyridine is stable to heating in acid but is rapidly destroyed under these conditions in the presence of persulfate.

The formation of 2-amino-5-nitrophenol from *p*-nitroaniline was measured similarly. The formation of *o*-aminophenol from aniline was measured by use of the Folin uric acid reagent.¹⁴ Ammonia was determined by direct Nesslerization.

Results

2-Aminopyridine was chosen as the model amine for these studies because of the ease of product determination.

1. Yield and Stoichiometry. Yield of material capable of reducing the Folin phenol reagent was examined as a function of the ratio of the reactants, of temperature, and of hydroxyl ion concentration. These results are summarized in Table I. All reactions were run for a sufficiently long time to consume at least 99% of the smaller component. The yield appears to be independent of temperature, but dependent on both the hydroxyl ion concentration and the ratio of the reactants.

Table I. Yield of 2-Amino-3-hydroxypyridine from the Reaction of Persulfate and 2-Aminopyridine

[2-AP] ^a	[S ₂ O ₈ ²⁻]	Ratio	[KOH]	Temp, °C	Yield, ^b %
0.0475	0.00250	19	0.5	40	56
0.0450	0.0050	9	0.5	40	52
0.0400	0.0100	4	0.5	40	45
0.0250	0.0250	1	0.5	40	29
0.0100	0.0400	0.25	0.5	40	4
0.200	0.0245	8.15	0.475	40	40.5
0.400	0.0387	10.2	0.475	30	41
0.400	0.0400	10	0.475	50	42.5
0.10	0.01	10	1.8	40	31
0.10	0.01	10	0.9	40	36
0.10	0.01	10	0.45	40	44
0.10	0.01	10	0.09	40	46
0.10	0.01	10	0.018	40	50

^a 2-AP is 2-aminopyridine. ^b Yield determinations are the averages of two runs.

The ultraviolet spectra of ether extracts of reaction mixtures were examined for the presence of 2-nitrosopyridine, 2-nitropyridine, 2,2'-azopyridine, and 2,2'-azoxypyridine. None of these materials was detected. Paper chromatography of reaction mixtures following acid hydrolysis revealed only one Folin-positive spot corresponding to 2-amino-3-hydroxypyridine, although a number of other unidentified ultraviolet-absorbing spots were present.

2. Order in Persulfate. At an amine:persulfate ratio of 10, the disappearance of persulfate followed apparent first-order kinetics for about 75% of the reaction, when the kinetics were examined as plots of the logarithm of persulfate concentrations *vs.* time; a negative deviation was evident thereafter. A typical plot is shown in Figure 1. If, however, successive *k*

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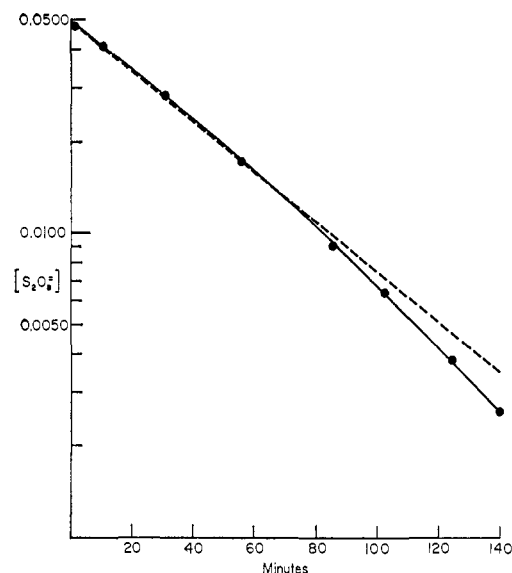


Figure 1. Rate plot for the oxidation of 2-aminopyridine by persulfate. Conditions were: 0.450 *N* KOH, 0.5 *M* 2-aminopyridine, 0.0501 *M* K₂S₂O₈, 40.0°. The solid line represents the experimental findings; the dotted line is straight.

values are computed, a steady drift to more negative values is evident. The drift during the first half of the reaction is less than 5%.

3. Order in Amine. Table II shows that the reaction is likewise first order in amine. We may thus write the rate law, $v = k[S_2O_8^{2-}][ArNH_2]$, at least for the major part of the reaction.

Table II. Order in 2-Aminopyridine^a

[2-AP]	[S ₂ O ₈ ²⁻]	<i>k</i> , l./mole min
0.040	0.0038	0.0403
0.100	0.010	0.0392
0.1062	0.010	(0.0402)
0.200	0.024	0.0404
0.300	0.0295	(0.0397)
0.400	0.030	0.0405

^a General conditions; 0.475 *M* KOH, 40.0°. 2-AP is 2-aminopyridine. *k* values were calculated by measurement of the pseudo-first-order rate constant during the first half-time of the reaction and division of this constant by 2-aminopyridine concentration. The values given are the averages of duplicate determinations with the exception of the values marked with parentheses, which are the result of single runs. The average *k* value is 0.0401.

4. pH Dependency. The variation of rate with pH is shown in Figure 2 and demonstrates that it is the unprotonated amine which is the reactive species. 2-Aminopyridine has a p*K*_a of 6.9. The ionic strength was constant within this series of experiments.

5. Salt Effects. Table III shows that there is a general and positive salt effect of rather small magnitude, as expected for a reaction between an ion and an uncharged molecule.

6. Activation Parameters. The variation of the rate constant with temperature is given in Table IV. The derived activation parameters are as follows: *E*_a = 15.7 ± 0.3 kcal/mole; Δ*S*[‡] = -25.5 ± 1 eu. These values are of the magnitude expected for nucleophilic displacement on peroxide oxygen.¹⁰

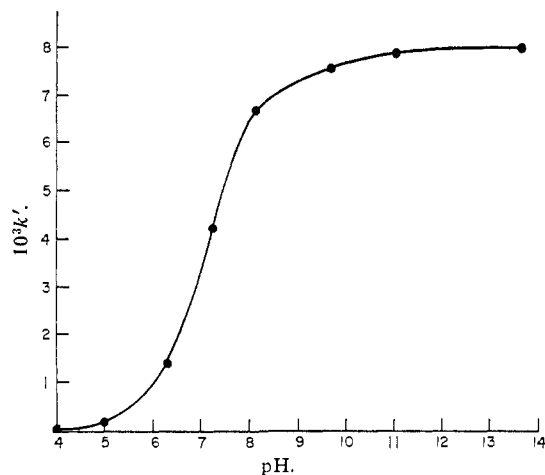


Figure 2. The effect of pH on the rate of oxidation of 2-aminopyridine by persulfate. General conditions were: 0.200 *M* 2-aminopyridine, 0.020 *M* persulfate, 40.0°. Buffers were added such that the ionic strength increment was equal to 0.475. The specific pH values and additions were: pH 13.7, KOH; pH 11.1, phosphate; pH 9.7, carbonate; pH 8.1, phosphate; pH 7.3, phosphate; pH 6.3, phosphate; pH 5.0, acetate; pH 4.0, acetate.

7. Effect of Radical Traps. Allyl acetate, an effective sulfate radical trap,¹⁵ had no effect on the rate of disappearance of persulfate in the presence of 2-aminopyridine at pH 7. The final yield of 2-amino-3-hydroxypyridine was likewise unaffected. The rate of

Table III. Salt Effects^a

Additions	<i>k</i> , l./mole min
No additions	0.0401
0.2 <i>M</i> NaCl	0.0415
0.5 <i>M</i> NaCl	0.0457
1.0 <i>M</i> NaCl	0.0535
2.0 <i>M</i> NaCl	0.0782
1/3 <i>M</i> Na ₂ SO ₄	0.0471
2/3 <i>M</i> Na ₂ SO ₄	0.0725
1 <i>M</i> KCl	0.0507
1 <i>M</i> NaClO ₄ ^b	0.0498

^a General conditions: 0.475 *M* KOH, 0.200 *M* 2-aminopyridine, 0.02 *M* persulfate, 40.0°. ^b For the reaction in the presence of sodium perchlorate, NaOH was substituted for KOH.

Table IV. Rate Dependence on Temperature^a

Temp, °C	<i>k</i> , l./mole min
50.0	0.0822
40.0	0.0401
30.0	0.0178
19.3	0.00665

^a General conditions: 0.475 *M* KOH, 0.400 *M* 2-aminopyridine, and 0.04 *M* persulfate.

disappearance of persulfate in the presence of *p*-nitroaniline at pH 7 was also unaffected by the presence of allyl acetate.

8. Effect of Substituents. Second-order constants for the reaction of persulfate with aniline, *p*-toluidine, and *p*-nitroaniline are presented in Table V. It is clear

Table V. The Effect of Substituents on the Rate of Oxidation of Anilines

Compound	Concn, <i>M</i>	Solv ^a	Temp, °C	<i>k</i> ', min ⁻¹	<i>k</i> , l./mole min
<i>p</i> -Nitroaniline	0.029	A	40.0	0.00326 ^b	0.113
<i>p</i> -Nitroaniline	0.029	B	40.0	0.00062 ^b	0.0215
Aniline	0.0302	B	40.0	0.0344	1.14
Aniline	0.0302	C	40.0	0.0764	2.53
Aniline	0.0121	C	40.0	0.0298	2.47
Aniline	0.0121	D	40.0	0.0297	2.46
Aniline	0.0302	C	30.0	0.0399	1.32
<i>p</i> -Toluidine	0.0300	C	30.0	0.101	3.36

^a Solvents: A, 0.475 *M* KOH in 24% 2-propanol; B, 0.04 *M* phosphate buffer, pH 7.0 in 24% 2-propanol; C, 0.04 *M* phosphate buffer, pH 7.0 in water; D, 0.1 *M* KOH in water. ^b These values have been corrected for the rate of oxidation of 2-propanol by subtracting 0.00018 from the pseudo-first-order rate constants.

that the reaction is accelerated by electron-releasing substituents. A Hammett plot of these data suggests a ρ value in the vicinity of -1.3 . This may be compared with the value of -1.86 reported for the reaction of aromatic amines with peroxyacetic acid,¹⁶ and of -1.58 for the reaction of nitrosobenzenes with peroxyacetic acid.¹⁷ The rate of oxidation of aniline is decreased by about a factor of two in 24% 2-propanol as compared with water as solvent. In accordance with the evidence that the reactive species of 2-aminopyridine is the unprotonated amine, the rate of oxidation of aniline ($pK_a = 4.6$) is the same at pH 7 and in 0.1 *M* KOH. *p*-Nitroaniline is oxidized more rapidly in 0.475 *M* KOH than at pH 7, but this is perhaps attributable to ionization to the anion.¹⁸

9. Site of Attack. Since aromatic amines are ambident nucleophiles, either attack at carbon or attack at nitrogen followed by rearrangement is *a priori* conceivable. Table VI compares the rates of oxidation of three sets of aromatic amines in which one *ortho* position is blocked and a common substituent is placed either *meta* to the amino group (*para* to the final position of the sulfate group) or *para* to the amino group (*meta* to the final position of the sulfate group). One isomer will react with persulfate faster on the hypothesis of rate-limiting electrophilic attack at nitrogen, the other on the assumption of rate-limiting electrophilic attack at carbon. For each set, the order of reactivity is that to be expected on the basis of rate-limiting attack at nitrogen, as shown by the values of the σ constants.

10. Rate of Oxidation of 2-Amino-3,5-dideuterio-pyridine. The rate of oxidation of this material by persulfate was identical with that of the undeuterated material. The yield of product at hydroxyl ion concentrations from 0.1 to 3 *M* as measured by the quantity of Folin-reactive material present following acid hydrolysis was likewise unaffected by deuteration.

11. Formation of Ammonia from 2-Aminopyridine and 2-Amino-3-hydroxypyridine. Considerable quantities of ammonia are produced during the oxidation of 2-aminopyridine by persulfate. At 2-aminopyridine: persulfate ratios between 100 and 10, in 0.9 *M* KOH

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(17) K. M. Ibne-Rasa, C. G. Lauro, and J. O. Edwards, *ibid.*, **85**, 1165 (1963).

(18) C. H. Rochester, *Trans. Faraday Soc.*, **59**, 2820 (1963).

(15) I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *J. Am. Chem. Soc.*, **75**, 1439 (1953).

Table VI. Comparison of the Rate of Oxidation of 2,3- and 2,4-Disubstituted Aromatic Amines by Persulfate Ions^a

Compound	Concn, M	k, min^{-1}	$k, \text{l./mole min}$
I. 2-Aminopyridine Series (0.475 M KOH in water)			
2-Amino-5-methylpyridine	0.1001	0.0184	0.183
2-Amino-5-methylpyridine	0.200	0.0380	0.190
2-Amino-6-methylpyridine	0.1001	0.00935	0.0934
2-Amino-6-methylpyridine	0.2023	0.0189	0.0935
Values for the methyl σ constants are: $\sigma_m = -0.069, \sigma_p^+ = -0.311$			
II. 2-Chloroaniline Series (0.04 M phosphate buffer, pH 7.0 in 24% 2-propanol)			
2,3-Dichloroaniline	0.0401	0.00276	0.0690
2,4-Dichloroaniline	0.0401	0.00538	0.134
Values for the chloro σ constants are: $\sigma_m = 0.373, \sigma_p^- = 0.114$			
III. 2-Methylaniline Series (0.04 M phosphate buffer, pH 7.3 in 24% 2-propanol)			
2-Methyl-4-nitroaniline	0.01505	0.000790	0.0525
2-Methyl-3-nitroaniline	0.01502	0.00350	0.233
Values for the nitro σ constants are: $\sigma_m = 0.710, \sigma_p^- = 1.27$			

^a All runs were conducted at 40.0°. The initial amine:persulfate ratio was 10 in all cases. Values for the σ constants are from J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 87-90.

at 40°, the molar ratio between ammonia produced and persulfate added is between 0.34 and 0.21. Thus roughly 30% of the persulfate added in these experiments, where the yield of 2-amino-3-pyridyl hydrogen sulfate is in the 45-55% range (see Table I), is consumed in reactions resulting in deamination. 2-Amino-3-hydroxypyridine reacts with persulfate at least 1000 times faster than 2-aminopyridine to give a quantitative yield of ammonia and oxidation products (see below). *o*-Aminophenol likewise gives a quantitative yield of ammonia, while aniline, like 2-aminopyridine, gives a yield of about 30%. 2-Amino-3-pyridyl hydrogen sulfate reacts with persulfate, but only at a rate about one-half that of 2-aminopyridine.

12. Formation of Material with the Properties of Synthetic Humic Acid. When an alkaline mixture of aniline and persulfate is acidified, a dark brown polymeric material precipitates. The ultraviolet spectrum in alkaline solution shows no peaks at wavelengths longer than 220 μ . The infrared spectrum is shown in Figure 3. Oxidation of *o*-aminophenol by persulfate under alkaline conditions produced a similar material whose infrared spectrum is shown for comparison in Figure 3. The spectra, although not identical, are closely similar. The oxidation of *o*-aminophenol by persulfate in alkali was described in 1925 by Eller.¹⁹ The product is a member of the class of materials known as synthetic humic acid. In quantitative terms, the oxidation of 1 mole of aniline by 0.1 mole of persulfate in 1 l. of 0.5 M KOH gave an isolated yield of 2.3 g of this polymer. These are conditions which give a 50-55% yield of *o*-aminoaryl sulfate so that the combined yield of sulfate ester and polymer amounts to roughly 75-80% of starting material.

Discussion

The evidence suggests rate-limiting electrophilic attack by the persulfate ion on nitrogen of the neutral amine

(19) W. Eller, *Ann.*, **442**, 173 (1925).

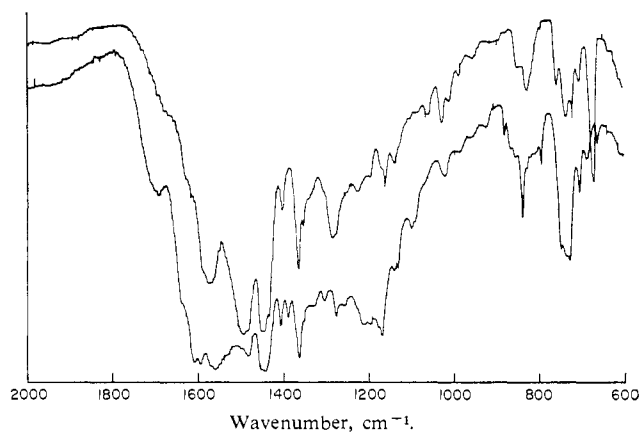


Figure 3. Infrared spectra of humic acids isolated from the persulfate oxidation of aniline (upper curve) and of *o*-aminophenol (lower curve). The spectra were taken in mineral oil mulls using a Perkin-Elmer Model 237B.

followed by rearrangement to the *o*-aminoaryl sulfate. Attack at nitrogen rather than at carbon is consistent with work in other systems.^{16,17,20-23} Haberfield and Paul have recently demonstrated the existence of an N-chloro intermediate in the chlorination of N-methylaniline.²⁴

The effect of substituents in the persulfate-aromatic amine reaction argues strongly for electrophilic attack at nitrogen. Initial attack at nitrogen also provides the rationale for the preferential *ortho* orientation. The absence of significant radical involvement is shown by the first-order dependence on both amine and persulfate and by the lack of effect of radical traps on either the rate of disappearance of persulfate or the yield of *o*-aminoaryl sulfate. The points of difficulty are the nature of the initial product resulting from attack of the peroxide on nitrogen and the fate of those molecules which do not appear as *o*-aminoaryl sulfate. If the attack were initially at nitrogen, a reasonable intermediate would be the arylhydroxylamine-O-sulfonate.

Salts of phenylhydroxylamine-O-sulfonate have been prepared by Boyland and Nery.²⁵ These authors report that phenylhydroxylamine O-sulfonate rearranges to *o*-aminophenyl sulfate on standing at room temperature in 2 N HCl. The paper states that salts of the various hydroxylaminesulfonic acids "are unchanged in 2% aqueous sodium hydrogen carbonate or 2 N ammonia after 16 hr at room temperature in the dark. . . ." and that "In hot 2 N sodium hydroxide they give complex mixtures containing *o*- and *p*-aminophenol, aniline, azoxybenzene, and unidentified products." Our attempts to demonstrate the presence of alkali-labile material in aniline-persulfate reactions run at neutrality were unsuccessful. However, Professor Boyland has informed me that although the N-acyl derivatives are stable, phenylhydroxylamine-O-sulfonic acid itself is unstable in solution at all pH values, that the potassium salt shows signs of decom-

(20) A. G. Davies, "Organic Peroxides," Butterworth and Co., Ltd., London, 1961, pp 135-136.

(21) D. B. Denney and D. Z. Denney, *J. Am. Chem. Soc.*, **82**, 1389 (1960).

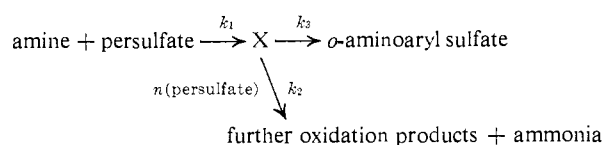
(22) D. M. Graham and R. B. Mesrobian, *Can. J. Chem.* **41**, 2938 (1963).

(23) W. B. Geiger, *J. Org. Chem.*, **23**, 298 (1958).

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(25) E. Boyland and R. Nery, *J. Chem. Soc.*, 5217 (1962).

position in the solid state at 0° after a few days, and that considerable rearrangement occurs during chromatography of the compound in neutral solvent systems.²⁶ Although we cannot say how the rate of rearrangement of the arylhydroxylamine-O-sulfonates to the *o*-aminoaryl sulfates varies as a function of pH, it appears that the O-sulfonates are at least not unreasonable intermediates in the reaction between aromatic amines and persulfate ions. Boyland and Nery also report that phenylhydroxylaminesulfonic acids (both O- and N-substituted compounds are discussed) reduce ammoniacal silver nitrate and Fehling's solution. Aniline does not reduce either solution. Phenylhydroxylamine-O-sulfonate is thus a better reducing agent than the parent amine. This is reasonable since the hydroxylamines are members of the class of nucleophiles which exhibit an enhanced degree of nucleophilic reactivity which has been termed the α effect by Edwards and Pearson.²⁷ This aspect of their expected behavior is consistent with their role as intermediates in the persulfate oxidation of aromatic amines and with the low yields of *o*-sulfates obtainable in the reaction. The postulated intermediate is more readily oxidized than the starting material. The yield of *o*-aminoaryl sulfate falls in strong alkali, a fact perhaps attributable to even more ready attack by persulfate on the dianion of the arylhydroxylamine-O-sulfonate. We may write a general scheme for the course of the reaction



where X may be the arylhydroxylamine-O-sulfonate. On the steady-state assumption, the ratio of the rate of formation of *o*-aminoaryl sulfate to the rate of formation of further oxidation products will be equal to $k_3/k_2[\text{persulfate}]^n$. This expression is then consistent with the dependence of the yield on the persulfate: amine ratio and also explains the deviation from first-order dependence on persulfate concentration.

(26) Letter from Professor Boyland.

(27) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

The major product of the reaction other than the *o*-aminoaryl sulfate is a polymer known as synthetic humic acid. Materials of this class were reported as products of the alkaline persulfate oxidation of dihydric phenols and aminophenols by Eller.^{19,28} Even monohydric phenols are oxidized to humic acids with persulfate: phenol ratios of 2 to 4.^{28b} These are conditions under which the phenol *p*-sulfate (the normal Elbs product) is formed in very low yield.¹¹ Ziechmann and Scholz²⁹ and Elofson³⁰ have reported spectroscopic characteristics of humic acids from a variety of sources which are thought to arise through condensation of hydroxyquinones.³¹ A substituted naphthoquinone imine of this oxidation level has been identified as a product of the persulfate oxidation of 2-naphthylamine.¹ Characterization of humic acids is difficult and we have not undertaken this task here. Recent reviews are available.^{32,33} It suffices for our purposes to have shown the close similarity between the polymeric material obtained from the oxidation of *o*-aminophenol, known to be oxidized to a humic acid by persulfate,¹⁹ and that obtained from aniline. A corresponding product is presumably obtained from 2-aminopyridine, but due to the ring nitrogen, it is soluble in acid and we have not isolated it.

The humic acid polymers should be distinguished from polymers of the aniline black-emeraldine type which result from homolytic coupling of aromatic amines in acid solution.³⁴

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