Revised Mechanism of Boyland–Sims Oxidation

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ABSTRACT: New computational insights into the mechanism of the Boyland–Sims oxidation of arylamines with peroxydisulfate $(S_2O_8^{2-})$ in an alkaline aqueous solution are presented. The key role of arylnitrenium cations, in the case of primary and secondary arylamines, and arylamine dications and immonium cations, in the case of tertiary arylamines, in the formation of corresponding *o*-aminoaryl sulfates, as prevalent soluble products, and oligoarylamines, as prevalent insoluble products, is proposed on the basis of the AM1 and RM1 computational study of the Boyland–Sims oxidation of aniline, ring-substituted (2-methylaniline, 3-methylaniline, 4-methylaniline, 2,6-dimethylaniline, 4-bromoaniline, 3-chloroaniline, and 2-nitroaniline) and N-substituted anilines (*N*-methylaniline, diphenylamine, and *N*,*N*-dimethylaniline). Arylnitrenium cations and



sulfate anions (SO_4^{2-}) are generated by rate-determining two-electron oxidation of primary and secondary arylamines with $S_2O_8^{2-}$, while arylamine dications/immonium cations and SO_4^{2-} are initially formed by two-electron oxidation of tertiary arylamines with $S_2O_8^{2-}$. The subsequent regioselectivity-determining reaction of arylnitrenium cations/arylamine dications/ immonium cations and SO_4^{2-} , within the solvent cage, is computationally found to lead to the prevalent formation of *o*-aminoaryl sulfates. The formation of insoluble precipitates during the Boyland–Sims oxidation of arylamines was also computationally studied.

INTRODUCTION

Although the Elbs peroxydisulfate oxidation of phenols in alkaline solution, leading to the prevalent formation of *p*-hydroxyaryl sulfates, had been known since 1893, it was not until six decades later that Boyland and Sims reported the extension of this reaction to arylamines.^{1–9} It was found that aminoaryl sulfates were the major soluble products of the oxidation of arylamines with $S_2O_8^{2-}$, but, unexpectedly, it was revealed that the substitution took place exclusively or predominantly at ortho position to the amino group. Primary, secondary, and tertiary arylamines (1, Scheme 1) are all converted to the corresponding *o*-aminoaryl sulfates (2, Scheme 1) under conditions similar to those used for the Elbs oxidation: room temperature or below, aqueous alkali, and equimolar quantities of arylamine and $S_2O_8^{2-}$. Subsequent hydrolysis with hot concentrated hydrochloric acid yields *o*-aminophenols (3, Scheme 1).

The rate law is $v = k[S_2O_8^{2-}][arylamine]$. The involvement of primary/secondary arylamine neutral radicals and tertiary arylamine cation radicals, as a highly reactive intermediate product of single-electron oxidation of arylamines in alkaline solution, in the formation of *o*-aminoaryl sulfates was excluded because radical traps have no effect on either the rate or extent of *o*-aminoaryl sulfate formation.^{6a} Arylnitrenium cations, as highly reactive intermediate products of two-electron oxidation of primary and secondary arylamines in a broad pH range, have not been considered during the decades as an alternative reactive species involved in the formation of *o*-aminoaryl sulfates simply because the arylnitrenium cation chemistry has become well understood only more than 40 years after the Boyland–Sims oxidation

Scheme 1. Boyland–Sims Oxidation of Aniline ($R^1 = R^2 = H$) and Its N-Alkyl/Aryl-Substituted Derivatives [Secondary ($R^1 = Alkyl/Aryl$, $R^2 = H$) and Tertiary Anilines (R^1 and $R^2 = Alkyl/Aryl$)] with $S_2O_8^{2-1}$



discovery.¹⁰ It was only noted by Behrman that "a nitrene mechanism is not consistent with the fact that tertiary anilines behave similarly to primary anilines".⁸ Since electron-releasing substituents at an aromatic ring accelerate the oxidation of arylamines with $S_2O_8^{2-}$, the nucleophilic displacement by the unprotonated amine nitrogen on peroxide oxygen of peroxydisulfate was proposed by Behrman as a rate-determining step.^{6a} In this case, the exclusive ortho orientation of the entering sulfate group could, according to Behrman, arise from attack of $S_2O_8^{2-}$ at the ortho carbon atom assisted by interaction with the amino group, nitrogen atom followed by rearrangement, or ipso carbon atom followed by rearrangement. Much conflicting kinetic and mechanistic evidence was collected.^{6,7} After decades of

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controversy,^{6,7} arylhydroxylamine-O-sulfonates were proposed by Behrman as the most probable intermediates, at least in the case of tertiary anilines,⁸ as a result of a nucleophilic displacement by the arylamine nitrogen on peroxide oxygen of peroxydisulfate. This was based on the experimental finding that arylhydroxylamine-O-sulfonate, formed by the reaction between N,N-dimethylaniline N-oxide and the sulfur trioxide-pyridine complex in dry pyridine, is stable enough to be isolated under anhydrous conditions at room temperature but rapidly rearranges upon the addition of water to a mixture of N,N-dimethylaniline o- and p-sulfates in the same ratio as is given by the peroxydisulfate oxidation of N,N-dimethylaniline in alkaline aqueous solution.8 However, the unambiguous evidence of Behrman's mechanism, which should be the isolation and identification of arylhydroxylamine-O-sulfonate intermediates upon the reaction of arylamines with peroxydisulfate under anhydrous conditions, is still missing.

We propose a key role of arylnitrenium cations in the formation of *o*-aminoaryl sulfates as prevalent soluble products and oligoarylamines as prevalent insoluble products in the Boyland-Sims oxidation of primary and secondary arylamines, based on the recent quantum chemical findings that arylnitrenium cations are formed in the initiation phase of the oxidation of primary arylamines with $S_2O_8^{2-}$ in an aqueous solution, when-ever the formation of *p*-/*o*-iminoquinonoid product is not possible.¹¹⁻¹⁵ We also propose a key role of arylamine dications and immonium cations in the mechanism of Boyland-Sims oxidation of tertiary arylamines. In the present contribution, the Boyland-Sims oxidation of aniline, 12 ring-substituted anilines (2-methylaniline, 3-methylaniline, 4-methylaniline, 2,6-dimethylaniline, anthranilic acid, 4-aminobenzoic acid, sulfanilic acid, sulfanilamide, 4-phenylaniline, 4-bromoaniline, 3-chloroaniline, and 2-nitroaniline), and three N-substituted anilines (N-methylaniline, diphenylamine, and N,N-dimethylaniline) was studied by AM1 and RM1 computational methods. The thermodynamic stabilities of aniline and 15 ring- and N-substituted anilines, and their reactive species (cation radicals, neutral radicals, nitrenium cations, and dications) in water, were computationally determined. The heats of 31 single-electron and 16 two-electron redox reactions of aniline/substituted anilines with $S_2 O_8^{2-}$ in aqueous solution (neutral and alkaline conditions), leading to the formation of arylamine cation radicals/neutral radicals and arylnitrenium cations/arylamine dications, were calculated. Exactly 75 reactions of arylnitrenium cations with SO_4^{2-} , $S_2O_8^{2-}$, parent arylamines, hydroxide anion (OH⁻), and water were computationally studied. The reactions of $N_{*}N$ -dimethylaniline dication and immonium cation with SO₄²⁻ were also theoretically studied. The thermodynamic stabilities of 280 intermediates were investigated. Semiempirical quantum chemical AM1 and RM1 results/ predictions were correlated with corresponding experimental kinetic and synthetic data for Boyland-Sims oxidation of aniline, ring-substituted anilines, and N-substituted anilines, collected during the past six decades.

COMPUTATIONAL METHODS

A semiempirical AM1 method¹⁶ (included in the molecular orbital program¹⁷ MOPAC 97, part of the Chem3D Pro 5.0 package, CambridgeSoft Corporation), and RM1 method¹⁸ (improved/reparametrized version of AM1, included in MO-PAC 2009) have been used to obtain the heat of formation (ΔH_f) of individual species. AM1 method was proved to be

Scheme 2. Single-Electron Oxidations of Aniline (C), Anilinium Cation (A), Aniline Cation Radical (D), and Aniline Neutral Radical (F), Accompanied by Corresponding Acid/Base Equilibria HB^+/B : Anilinium Cation/Aniline, Anilinium Dication Radical (B)/Aniline Cation Radical, Aniline Cation Radical/Aniline Neutral Radical, Aniline Dication (E)/Aniline Nitrenium Cation (G), and Aniline Nitrenium Cation/Aniline Nitrene (I, Singlet Nitrene)



accurate enough to have useful predictive power, and fast enough to allow the processing of large molecules such as aromatic amine oligomers and their intermediates.^{15,19} In a recent computational study focused on the torsion angle between rings, known to affect strongly the electronic and optical properties of conjugated polymers, Dávila et al. suggested that the AM1 method is preferred over the PM3 for ring-structured oligomeric chains.¹⁹ Exactly 280 intermediates, formed in reactions of nitrenium cations/dications/immonium cations of aniline and substituted primary, secondary, and tertiary anilines with SO_4^{2-} , $S_2O_8^{2-}$, OH^- , H_2O , and aniline/substituted anilines in an alkaline aqueous solution, were computationally processed in the present study. Our previous computational study¹¹ has clearly shown the crucial influence of solvation on the acid-base and redox properties of aniline, its reactive species, and oligomers. Therefore, solvation effects were taken into account using the conductor-like screening model (COSMO) to approximate the effect of water surrounding the molecule.²⁰ Conformational analysis of all intermediates is done. The steric energy was minimized using the MM2 molecular mechanics force-field method.²¹ Input files for the semiempirical quantum chemical computations of all intermediates were the most stable conformers of investigated molecular structures. The geometry optimization was performed by the EigenFollowing procedure.^{22,23} The restricted Hartree-Fock method has been used for the molecular structures, and the unrestricted Hartree-Fock method has been used for radical species.

RESULTS AND DISCUSSION

Reactions of aniline with oxidizing agents proceed in two fundamentally different ways. The oxidizing agent can either donate oxygen to the aniline molecule or it can remove electron-(s)/hydrogen from the aniline molecule.²⁴ Well-known efficient oxygen donors are hydrogen peroxide, perphosphoric acid, Table 1. Heats of Formation, ΔH_f (kcal mol⁻¹), of Aniline and Ring/N-Substituted Anilines, and Their Reactive Species Formed by Single-Electron Oxidation (Arylamine Cation Radicals, ArNH₂⁺⁺/[ArNHR]⁺⁺, and Neutral Radicals, ArNH⁺/[ArNR]⁺) and Two-Electron Oxidation (Arylamine Nitrenium Cations, ArNH⁺/[ArNR]⁺) in Aqueous Solution, Computed by AM1/COSMO and RM1/COSMO Methods

	$\Delta H_{\rm f} (\rm kcal \ mol^{-1})$							
	ArNH ₂ /ArNHR		ArNH2 ^{•+} /	$ArNH_2^{\bullet+}/[ArNHR]^{\bullet+}$ ArN		/[ArNR]•	ArNH ⁺	/[ArNR] ⁺
arylamine	AM1	RM1	AM1	RM1	AM1	RM1	AM1	RM1
aniline	11.38	12.30	143.34	130.14	55.31	47.59	185.59	189.02
2-methylaniline	6.69	3.98	136.01	121.35	48.65	38.68	177.00	177.52
3-methylaniline	6.18	2.68	136.17	120.63	48.01	38.13	179.18	180.65
4-methylaniline	6.30	3.23	134.32	119.50	46.69	37.51	175.16	175.35
2,6-dimethylaniline	-0.32	-4.10	128.99	112.93	40.74	29.65	168.84	167.03
2-carboxyaniline (anthranilate anion)	-180.93	-167.99	-46.61	-50.90	-139.23	-132.43	-5.91	8.83
4-carboxyaniline (4-aminobenzoate anion)	-181.79	-168.47	-47.93	-49.62	-137.43	-131.93	-5.85	8.87
4-sulfoaniline (sulfanilate anion)	-245.10	-243.81	-104.63	-114.03	-196.25	-199.02	-57.09	-44.50
4-sulfamoylaniline (sulfanilamide)	-90.36	-106.78	54.23	29.69	-37.91	-52.85	101.58	103.05
4-phenylaniline	34.10	32.93	167.43	150.43	78.65	67.94	207.98	206.70
4-bromoaniline	14.35	14.23	149.81	136.15	59.73	51.54	195.51	198.59
3-chloroaniline	6.03	1.69	138.76	124.10	49.02	38.89	182.94	186.68
2-nitroaniline	4.14	0.93	146.83	132.65	51.44	42.47	192.92	195.18
N-methylaniline	18.36	16.98	149.09	133.97	54.72	42.04	184.64	183.16
N-phenylaniline (diphenylamine)	47.30	42.30	184.59	163.02	85.86	67.96	216.65	210.72

Table 2. Heats of Single-Electron and Two-Electron Redox Reactions, ΔH_r (kcal mol⁻¹), of Aniline and Substituted Primary (ArNHR, R = H) and Secondary Anilines (ArNHR, R = Alkyl, Aryl) with Peroxydisulfate in an Alkaline Aqueous Solution, Leading to the Formation of Neutral Radicals [ArNR][•] and Nitrenium Cations [ArNR]⁺, Respectively, Computed by AM1/COSMO and RM1/COSMO Methods

	$\Delta H_{ m r}~(m kcal~mol^{-1})$					
	$ArNHR + S_2O_8^{2-} + OH^- \rightarrow$ $[ArNR]^{\bullet} + SO_4^{\bullet-} + SO_4^{2-} + H_2O$		$ArNHR + S_2 G$ $[ArNR]^+ + 2$	$D_8^{2-} + OH^- \rightarrow$ $2SO_4^{2-} + H_2O$		
arylamine	AM1	RM1	AM1	RM1		
aniline	-12.20	-30.57	-52.10	-48.14		
2-methylaniline	-14.17	-31.16	-56.00	-51.32		
3-methylaniline	-14.30	-30.41	-53.31	-46.89		
4-methylaniline	-15.74	-31.58	-57.45	-52.74		
2,6-dimethylaniline	-15.07	-32.11	-57.15	-53.73		
2-carboxyaniline (anthranilate anion)	-14.43	-30.30	-51.29	-48.04		
4-carboxyaniline (4-aminobenzoate anion)	-11.77	-29.32	-50.37	-47.52		
4-sulfoaniline (sulfanilate anion)	-7.28	-21.07	-38.30	-25.55		
4-sulfamoylaniline (sulfanilamide)	-3.68	-11.93	-34.37	-15.03		
4-phenylaniline	-11.58	-30.85	-52.43	-51.09		
4-bromoaniline	-10.75	-28.55	-45.15	-40.50		
3-chloroaniline	-13.14	-28.66	-49.40	-39.87		
2-nitroaniline	-8.83	-24.32	-37.53	-30.61		
N-methylaniline	-19.77	-40.80	-60.03	-58.68		
N-phenylaniline (diphenylamine)	-17.57	-40.20	-56.96	-56.44		

Caro's acid (peroxomonosulfuric acid), and percarboxylic acids (peracetic, trifluoroperacetic, perbenzoic, etc.).²⁴ Peroxydisulfate anion is one of the most powerful electron acceptors $(+2.0-2.1 \text{ V vs NHE}).^{25}$ Depending on the reductant nature, $S_2O_8^{2-}$ behaves as the single-electron oxidant $(\text{Fe}^{2+} + S_2O_8^{2-} \rightarrow$

 $Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-}$, $Cl^- + S_2O_8^{2-} \rightarrow Cl^{\bullet} + SO_4^{\bullet-} + SO_4^{2-}$) or two-electron oxidant $(Pb^{2+} + S_2O_8^{2-} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2SO_4^{2-})$. Since arylamines were proved to be easily oxidized by the mild single-electron oxidants which cannot donate oxygen $(Fe^{3+}, +0.77 \text{ V vs NHE})$,²⁵ leading thus to the

Scheme 3. Two-Electron Oxidation of Benzidine with Peroxydisulfate, Leading to the Formation of Diprotonated and Monoprotonated Iminobenzoquinonoid Form of Benzidine



undisputable formation of corresponding arylamine cation radicals, it was tentatively proposed in numerous papers published in the field of conducting polymers during the past two decades that the arylamine cation radicals are formed in the initiation phase of the oxidative polymerization of arylamines with strong oxidant $S_2O_8^{2-}$. Contrary to this frequently used incorrect tentative mechanistic scheme, which neglected Behrman's radical trap experiments in Boyland–Sims oxidation,^{6a} we have computationally confirmed in our previous studies^{11–15} that arylnitrenium cations, hydrated protons, and sulfate anions (reactions 1 and 2) are initial products of the two-electron oxidation of primary and secondary arylamines with $S_2O_8^{2-}$ in aqueous solution.

$$ArNH_{2(aq)} + S_2O_8^{2-}{}_{(aq)} \rightarrow [ArNH]^+{}_{(aq)} + H^+{}_{(aq)} + 2SO_4^{2-}{}_{(aq)}$$
(1)

$$ArNHR_{(aq)} + S_2O_8^{2-}_{(aq)} \rightarrow [ArNR]^+_{(aq)} + H^+_{(aq)} + 2SO_4^{2-}_{(aq)}$$
(2)

It should be noted here that two decades ago, on the basis of Genies and Lapkowski's spectroelectrochemical evidence²⁶ of the initial formation of aniline nitrenium cations during the anodic oxidation of aniline, Wei et al. tentatively proposed the initial formation of aniline nitrenium cations in the oxidative polymerization of aniline with $S_2O_8^{2-}$ under acidic reactive conditions.²⁷ They proved the prevalent formation of 4-amino-diphenylamine in the dimerization phase and tentatively proposed its formation through electrophilic aromatic substitution reaction of aniline with $C_6H_5NH^{+27}$

Scheme 4. Formation of Possible Intermediates in the Boyland–Sims Oxidation of Aniline, According to the Classic Behrman's Mechanism



Our computations have proved,¹¹ based on the modified Epiotis constraint $|E_{HOMO(D)} - E_{LUMO(A)}| < |E_{HOMO(A)} - E_{LUMO(D)}|$ ["D" represents an electron donor (reductant) and "A" stands for an electron acceptor (oxidant)],²⁸ that species formed by single-electron oxidation of aniline $[C_6H_5NH_2^{\bullet+}/C_6H_5NH^{\bullet+}, pK_a(C_6H_5NH_2^{\bullet+}) = 7.1$, Scheme 2]²⁹ can be easily oxidized with SO₄^{\bullet-}, which is a stronger oxidant (2.5–3.1 V vs NHE)³⁰ compared with S₂O₈²⁻. It follows that aniline oxidation in aqueous solution with S₂O₈²⁻ does not stop after single-electron transfer (reactions 3 and 4) but proceeds further, i.e., leads to the nitrenium cation in the initiation phase (reactions 5 and 6).

$$C_{6}H_{5}NH_{2(aq)} + S_{2}O_{8}^{2^{-}}{}_{(aq)} \rightarrow C_{6}H_{5}NH_{2}^{\bullet^{+}}{}_{(aq)} + SO_{4}^{\bullet^{-}}{}_{(aq)} + SO_{4}^{2^{-}}{}_{(aq)}$$
(3)

$$C_{6}H_{5}NH_{2(aq)} + S_{2}O_{8}^{2^{-}}{}_{(aq)} + OH^{-}{}_{(aq)} \rightarrow C_{6}H_{5}NH^{\bullet}{}_{(aq)} + SO_{4}^{\bullet^{-}}{}_{(aq)} + SO_{4}^{2^{-}}{}_{(aq)} + H_{2}O_{(aq)}$$
(4)

$$C_{6}H_{5}NH_{2}^{\bullet+}{}_{(aq)} + SO_{4}^{\bullet-}{}_{(aq)} \rightarrow C_{6}H_{5}NH^{+}{}_{(aq)} + H^{+}{}_{(aq)} + SO_{4}{}^{2-}{}_{(aq)}$$
(5)

$$C_{6}H_{5}NH^{\bullet}{}_{(aq)} + SO_{4}^{\bullet-}{}_{(aq)} \rightarrow C_{6}H_{5}NH^{+}{}_{(aq)} + SO_{4}^{2-}{}_{(aq)}$$
(6)

Acid—base properties of aniline nitrenium cation¹⁰ indicate that it is a very weak acid in water, $pK_a > 12.4$, in its deprotonation to corresponding nitrene (Scheme 2). It is also a weak base accepting a proton to form the aniline dication (Scheme 2), $pK_b > 13.0$. It can be concluded that the generation of aniline nitrenium cation is the common feature of all known aniline oxidations with $S_2O_8^{2-}$ in the very broad pH range, in the

Scheme 5. Formation of Prevalent Products (4, 7, 12-14), through the Most Stable Intermediates (5, 6, 9-11), in Reactions of Aniline Nitrenium Cation (8) with SO₄²⁻, S₂O₈²⁻, Aniline, OH⁻, and H₂O



presence of nonoxidizable acids/salts (sulfuric acid/sulfates/ hydrogen sulfates, etc.). Side reactions in the initiation phase, which can lead to the formation of $C_6H_5NH_2^{\bullet+}/C_6H_5NH^{\bullet}$, must be taken into account in the case of oxidizable acids/salts such as hydrochloric acid/chlorides (reactions 7–9).¹²

$$Cl^{-}_{(aq)} + S_2O_8^{2-}_{(aq)} \rightarrow Cl^{\bullet}_{(aq)} + SO_4^{\bullet-}_{(aq)} + SO_4^{2-}_{(aq)}$$
 (7)

$$C_{6}H_{5}NH_{2(aq)} + SO_{4}^{\bullet-}{}_{(aq)} \rightarrow C_{6}H_{5}NH_{2}^{\bullet+}{}_{(aq)} + SO_{4}^{2-}{}_{(aq)}$$
(8)

$$C_6H_5NH_{2(aq)} + Cl^{\bullet}_{(aq)} \rightarrow C_6H_5NH_2^{\bullet+}_{(aq)} + Cl^{-}_{(aq)}$$
(9)

In the present study we computed (AM1/COSMO, RM1/ COSMO) the heats of formation, $\Delta H_{\rm fr}$ of aniline and 14 ring-/*N*substituted anilines in aqueous solution, as well as the heats of formation of their reactive species formed by single-electron oxidation (arylamine cation radicals and neutral radicals) and two-electron oxidation (arylamine nitrenium cations) (Table 1). On the basis of these data, accompanied by the computed data for the heats of formation of $S_2O_8^{2-}$ (-569.23 kcal mol⁻¹ AM1/ COSMO; -530.84 kcal mol⁻¹ RM1/COSMO), SO_4^{2-} (-432.27 kcal mol⁻¹ AM1/COSMO; -399.42 kcal mol⁻¹ RM1/COSMO), $SO_4^{\bullet-}$ (-262.09 kcal mol⁻¹ AM1/COSMO; -240.42 kcal mol⁻¹ RM1/COSMO), H_3O^+ (43.28 kcal mol⁻¹ AM1/COSMO; 47.23 kcal mol⁻¹ RM1/COSMO), H₂O (-68.44 kcal mol⁻¹ AM1/COSMO; -62.97 kcal mol⁻ RM1/COSMO), and OH^- (-137.44 kcal mol⁻¹ AM1/COS-MO; -106.11 kcal mol⁻¹ RM1/COSMO) in aqueous solution, we calculated the heats of single-electron and two-electron redox reactions of aniline and substituted primary and secondary anilines with peroxydisulfate in aqueous solution (neutral and alkaline conditions), $\Delta H_{\rm r}$, leading to the formation of arylamine cation radicals/neutral radicals and nitrenium cations, respectively (Table 2, data for classic Boyland-Sims alkaline conditions). Thus we provide additional semiempirical quantum chemical evidence that two-electron oxidation in Boyland-Sims oxidation of primary and secondary arylamines, leading to arylnitrenium cations, is generally thermodynamically more favorable than single-electron oxidation (Table 2). It is open to discussion whether the formation of arylnitrenium cations includes two sequential single-electron transfers and welldefined deprotonation steps (e.g., in alkaline solutions of aniline, $\mathbf{C} \rightarrow \mathbf{D} \rightarrow \mathbf{E} \rightarrow \mathbf{G}$, or $\mathbf{C} \rightarrow \mathbf{D} \rightarrow \mathbf{F} \rightarrow \mathbf{G}$, Scheme 2), or arylnitrenium cations are formed through concerted twoelectron transfer accompanied by deprotonation. Radical trap experiments^{6a} indicate that the concerted mechanism is more probable.

It is well-known that arylamines, such as benzidine, 4-aminodiphenylamine, etc., are not susceptible to the Boyland-Sims oxidation, i.e., cannot be transformed to o-aminoaryl sulfates, but rather give iminoquinonoid compounds upon two-electron oxidation with $S_2O_8^{2-}$ (Scheme 3).¹⁻⁹ Classic Behrman's mechanism cannot explain this phenomenon, since the E_i of benzidine ($E_i = 7.95$ eV AM1/COSMO) and similar compounds is not significantly lower in comparison with other arylamines which are susceptible to the Boyland-Sims oxidation (e.g., 1-aminonaphthalene, $E_i = 8.18 \text{ eV AM1/COSMO}$). According to our mechanism, this is due to the fact that nitrenium cations of benzidine/4-aminodiphenylamine type of arylamines are not real molecular species but represent unfavorable canonical forms (minor contributors) of resonance hybrids of monoprotonated forms of corresponding iminoquinonoid compounds (Scheme 3).¹¹ All the observed substitutent effects^{6a,c,7,31} are consistent with

our mechanism which proposes the two-electron oxidation of arylamine as a rate-determining step. The fact that electronreleasing substituents at an aromatic ring accelerate the oxidation of arylamines with $S_2 O_8^{2-}$ stems from the increased oxidizability, i.e., decreased ionization potentials, of ring-substituted arylamines which have electron-releasing substituents, in comparison with corresponding nonsubstituted arylamines. Also, it was observed that the rates of oxidation of 2-amino-5-methylpyridine, 2,4-dichloroaniline, and 2-methyl-3-nitroaniline are higher than those of 2-amino-6-methylpyridine, 2,3-dichloroaniline, and 2-methyl-4-nitroaniline, respectively.^{6a} On the basis of the values for the methyl, chloro, and nitro σ constants, Behrman has concluded that this kinetic finding excludes a nucleophilic displacement by the carbon (whether C2 or C4) of ring-/Nsubstituted aniline on the peroxide oxygen of $S_2O_8^{-2-}$, and indicates a nucleophilic displacement by the unprotonated amine nitrogen on the peroxide oxygen of $S_2O_8^{2-.6a}$ However, this conclusion is contradictory to Behrman's mechanism, because our AM1/COS-MO computations of the heats of formation of Behrman's proposed intermediates (Scheme 4) have shown that N-O intermediates are much more unstable than all other C1-O (ipso-attack), C2(6)-O (ortho-attack), and C4-O (para-attack) Table 3. Heats of Formation, $\Delta H_{\rm f}$ (kcal mol⁻¹), of the Intermediates [ArNR]OSO₃⁻ Formed in the Reaction of Nitrenium Cations of Aniline and Substituted Primary (R = H) and Secondary Anilines (R = Alkyl, Aryl) with SO₄²⁻ in an Alkaline Aqueous Solution, Computed by AM1/COSMO and RM1/COSMO Methods

	$\Delta H_{\rm f}([{ m ArNR}]{ m OSO_3}^-)$ (kcal mol ⁻¹)						
		AM1/COSMO					
arylamine	N-O	C2(6)-O	C4-0	N-O	C2(6)-O	C4-0	
aniline	-261.76	-273.00	-272.00	-241.34	-249.63	-248.82	
2-methylaniline	-269.87	C6-277.59	-276.06	-249.74	C6-257.26	-256.38	
3-methylaniline	-270.26	C2-277.06	-276.27	-250.74	C2-257.79	-257.30	
		C6-280.30			C6-259.48		
4-methylaniline	-268.98	-280.64	_	-250.73	-259.34	_	
2,6-dimethylaniline	-271.74	_	-283.85	-253.93	_	-267.02	
2-carboxyaniline (anthranilate anion)	-448.78	C6-465.61	-465.34	-419.51	C6 -428.70	-428.06	
4-carboxyaniline (4-aminobenzoate anion)	-456.44	-465.15	—	-420.97	-429.11	-	
4-sulfoaniline (sulfanilate anion)	-517.09	-526.03	—	-491.80	-498.22	-	
4-sulfamoylaniline (sulfanilamide)	-362.37	-368.10	—	-353.88	-355.73	-	
4-phenylaniline	-236.74	-249.18	—	-219.59	-228.40	-	
4-bromoaniline	-257.58	-268.24	_	-238.31	-245.71	_	
3-chloroaniline	-268.81	C2-276.60	-275.73	-249.39	C2-257.16	-255.83	
		C6-278.99			C6 -257.87		
2-nitroaniline	-267.33	C6-276.54	-274.94	-248.33	C6-257.28	-255.36	
N-methylaniline	-253.34	-270.36	-270.01	-241.00	-252.12	-251.80	
N-phenylaniline (diphenylamine)	-216.60	-239.62	-239.19	-208.98	-225.01	-224.83	

possible intermediates, e.g., in the case of aniline: $\Delta H_{f(N-O)} = -155.07$ kcal mol⁻¹, $\Delta H_{f(C1-O)} = -157.64$ kcal mol⁻¹, $\Delta H_{f[C2(6)-O]} = -181.93$ kcal mol⁻¹, and $\Delta H_{f(C4-O)} = -183.12$ kcal mol⁻¹. In accordance with our mechanistic scheme, we claim that observed differences in reactivity are simply due to the fact that 2-amino-5-methylpyridine ($E_i = 8.65 \text{ eV}$), 2,4-dichloroaniline ($E_i = 8.59 \text{ eV}$), and 2-methyl-3-nitroaniline ($E_i = 8.68 \text{ eV}$) are more oxidizable; i.e., they have lower energy of ionization than 2-amino-6-methylpyridine ($E_i = 8.76 \text{ eV}$), 2,3-dichloroaniline ($E_i = 9.11 \text{ eV}$), and 2-methyl-4-nitroaniline ($E_i = 8.83 \text{ eV}$), respectively, as determined by AM1/COSMO method. The rate of reaction of 2,4- and 2,6-disubstituted anilines (e.g., 2,4- and 2,6-dimethylaniline) with S₂O₈²⁻ is nearly the same for both isomers⁸ because of their nearly the same oxidizability, i.e., ionization potential.

Generated arylnitrenium cations are highly reactive electrophilic species. The positive charge distribution on the aniline nitrenium cation, represented by its resonance hybrid (8, Scheme 5), indicates that N, C2(6), and C4 are the main aniline/ substituted aniline nitrenium cation reactive centers. The primary targets for electrophilic attack of nitrenium cations are sulfate anions (Scheme 5), simultaneously formed within the same solvent cage. We propose that this is a major reaction route to aminoaryl sulfates. The reaction of arylnitrenium cation with SO4²⁻ represents a regioselectivity-determining step in the Boyland-Sims oxidation. The regioselectivity of the coupling reactions of nitrenium cations of aniline and ring-substituted primary and secondary anilines with SO4²⁻, according to the Hammond postulate,³² is governed by the stability of intermediates (Table 3, Scheme 6, Figure 1) resembling structurally the corresponding transition states. Our computational results are found to be consistent with all available experimental evidence.¹⁻⁹ It is proved by both AM1/COSMO and RM1/

COSMO methods (Table 1) that the most stable intermediates are formed by the C2(6) $-O-SO_3^-$ couplings. In excellent agreement with Boyland and Sims's experimental findings¹⁻⁹ in the case of meta-substituted anilines such as 3-methylaniline and 3-chloroaniline, which have unsymmetrical ortho positions, corresponding C6 $-O-SO_3^-$ coupled aminoaryl sulfates are computationally proved to be major products (Table 3). If both ortho positions are blocked by substituents, e.g., 2,6-dimethylaniline, calculations confirmed known experimental finding that para substitution rather than N substitution takes place (Table 3).

Both AM1/COSMO and RM1/COSMO computations show that reactions between arylnitrenium cations and sulfate anions, leading to the formation of the most stable intermediates $(C4-O-SO_3^- \text{ coupled intermediate in the case of 2,6-dimethyl$ $aniline and C2(6)-O-SO_3^- coupled intermediates in all other$ cases) are generally exothermic processes (Table 4). The subsequent rearrangement of formed intermediates to final aminoaryl sulfates is also generally exothermic (Table 4). Based on thesethermodynamic data, a general reaction diagram of the Boyland-Sims oxidation of primary and secondary arylamines can be drawn(Figure 2).

It is important to note that, in accordance with experimental results,⁸ the formation of a substantial amount of para-substituted products besides the ortho-substituted products is computationally confirmed, especially in the case of anthranilic acid oxidation³ (Table 3). Taking into account the differences in the heats of formation ($\Delta H_{f,C4-O-SO_3^-} - \Delta H_{f,C2(6)-O-SO_3^-}$, Table 3) of C4–O–SO₃⁻ and C2(6)–O–SO₃⁻ coupled intermediates, and assuming that these values correspond well to the differences in energy of C4–O–SO₃⁻ and C2(6)–O–SO₃⁻ it ransition states ($E_{a,C4-O-SO_3^-} - E_{a,C2(6)-O-SO_3^-}$), the ratio of rate constants $k_{C2(6)-O-SO_3^-}/k_{C4-O-SO_3^-}$ at T = 298 K could be

Scheme 6. Computationally Studied Intermediates in Reactions of Arylnitrenium Cations with $SO_4^{2-} (X = OSO_3^{-}), S_2O_8^{2-} (X = OS_2O_7^{-}), OH^- (X = OH), and H_2O (X = ^+OH_2)$



calculated (Table 5), since $A_{C2(6)-O-SO_3^-} \approx A_{C4-O-SO_3^-}$, as follows:

$$\frac{k_{C2(6)-O-SO_3^-}}{k_{C4-O-SO_3^-}} = \frac{A_{C2(6)-O-SO_3^-}}{A_{C4-O-SO_3^-}}$$
$$\exp[(E_{a,C4-O-SO_3^-} - E_{a,C2(6)-O-SO_3^-})/RT]$$
$$\cong \exp[(\Delta H_{f,C4-O-SO_3^-} - \Delta H_{f,C2(6)-O-SO_3^-})/RT]$$

In the case of aniline $(k_{C2(6)-O-SO_3^-}/k_{C4-O-SO_3^-} = 3.93)$, since there are two ortho positions to one para position, it can be calculated that ~88.7% *o*-aminophenyl sulfate and ~11.3% *p*-aminophenyl sulfate are predicted to be formed.

In accordance with experimental observations on the low stability of phenylhydroxylamine-O-sulfonate³³ and other arylhydroxylamine-O-sulfonates,³⁴ all our computations (Table 3) indicate that arylhydroxylamine-O-sulfonate intermediates (29, Figure 1) formed by N $-O-SO_3^-$ couplings are quite unstable, i.e., are much more unstable than both C2-(6) $-O-SO_3^-$ and C4 $-O-SO_3^-$ coupled intermediates. It follows that arylhydroxylamine-O-sulfonate intermediates are formed in negligible quantities during the Boyland–Sims oxidation. We propose that the low thermodynamic stability of arylhydroxylamine-O-sulfonates, as determined by our

computations, is the reason for their well-known facile transformation to the corresponding o-aminoaryl sulfates, 33,34 most probably by a rapid heterolytic dissociation to arylnitrenium cations and SO_4^{2-} , followed by formation of the lower energy intermediates (30, Figure 1) which then yield oaminoaryl sulfates. We suppose that high polar solvents, such as water, promote heterolytic dissociation of arylhydroxylamine-O-sulfonates to arylnitrenium cations and SO_4^{2-} , similarly to what was experimentally evidenced in the case of $4\text{-PhC}_6\text{H}_4\text{NHOCOtBu}^{10}$ and protonated arylhydroxylamines, e.g., PhNHOH₂^{+,10} It follows that experimentally evidenced^{8,33,34} rapid transformation of arylhydroxylamine-O-sulfonates to the oaminoaryl sulfates in aqueous solution do not represent crucial proof of their intermediacy in Boyland-Sims oxidation, as proposed by Behrman,^{6a,8} but only represent unequivocal experimental proof of rather low thermodynamic stability of arylhydroxylamine-O-sulfonates, computationally confirmed in the present study.

The reactions of arylnitrenium cations with $S_2O_8^{2-}$ in the bulk of an aqueous solution, followed by the reductive decomposition of formed aminoaryl peroxydisulfates, can also lead to aminoaryl sulfates (4 \rightarrow 7, Scheme 5). C2(6)–O–S₂O₇⁻ coupled intermediates were proved to be prevalent in the reactions of nitrenium cations of aniline and ring-substituted primary and secondary anilines with S₂O₈²⁻ (Table 6). Computational study of the stabilities of investigated 80 intermediates of aminoaryl sulfates and peroxydisulfates (Tables 3 and 6, Scheme 6) revealed their stabilization through intramolecular C_{ring} -H···O_{sulfate/peroxydisulfate} and N-H···



Figure 1. N–O, C2(6)–O, and C4–O coupled intermediates in reactions of aniline nitrenium cation with SO_4^{2-} and $S_2O_8^{2-}$ (32–34).

 $O_{sulfate/peroxydisulfate}$ hydrogen bonding (Figure 1), where C_{ring} represents C2(6) and/or C4, with the exception of N–O coupled intermediate of aminoaryl sulfate. The unusual C_{ring} –H···O_{sulfate/peroxydisulfate} hydrogen bonding in the intermediate is due to the high polarization of a corresponding C_{ring} –H bond, i.e., high acidity of a hydrogen atom which is bonded to the C2(6) atom and/or C4 atom attacked by the sulfate/peroxydisulfate anion.

Overall yields of aminoaryl sulfates are significantly lower than those of hydroxyaryl sulfates in the Elbs oxidation, especially in the case of primary and secondary arylamines (5-30%), due to the competitive oxidative polymerizations of arylamines which lead to the formation of insoluble, brown, amorphous materials.^{1–9} Although these precipitates were described in many papers as humic acid-like polymers, synthetic organic chemists paid no attention to their structural characterization since these precipitates were considered as an unwilling byproduct of aminoaryl sulfates in the Boyland-Sims oxidation.¹⁻⁹ On the other side, scientists working in the field of conducting polymers became interested in the elucidation of the molecular structure of these oligoarylamines, e.g., oligoaniline,^{35–39} because recent studies have revealed the crucial template function of in situ formed oligoanilines in the synthesis of polyaniline nanotubes, nanorods, and nanosheets, by the oxidative polymerization of aniline with ammonium peroxydisulfate under decreasing pH conditions (start in alkaline/slightly acidic solutions and finish at pH <2.0).^{35,40-42} We propose that the reaction between arylamine and its nitrenium cation¹¹⁻¹⁵ ($8 \rightarrow 9 \rightarrow 12$, Scheme 5) represents a general dimerization route in the oxidative oligomerization of primary and secondary arylamines with $S_2O_8^{-2}$ whenever the formation of iminoquinonoid compound by the two-electron oxidation of arylamine is not possible. The regioselectivity of the coupling reactions of aniline and ring-substituted primary and secondary anilines with their nitrenium cations in an

Table 4. Heats of Reaction, ΔH_r (kcal mol⁻¹), of AryInitrenium Cations [ArNR]⁺ of Aniline and Substituted Primary (R = H) and Secondary Anilines (R = Alkyl, Aryl) with Sulfate Anions in Alkaline Aqueous Solution, Leading to the Formation of the Most Stable Intermediates ([ArNR]OSO₃⁻, C4–O–SO₃⁻ Coupled Intermediate in the Case of 2,6-Dimethylaniline, and C2-(6)–O–SO₃⁻ Coupled Intermediates in All Other Cases), Computed by AM1/COSMO and RM1/COSMO Methods; Also, Heats of Reaction, ΔH_r (kcal mol⁻¹), of Subsequent Rearrangements of Formed Intermediates to Final Aminoaryl Sulfates

	ΔH_r (kcal mol ⁻)						
	$[ArNR]^+ + SO_4^{2-} \rightarrow [ArNR]OSO_3^-$ intermediate		$[ArNR]OSO_3^-$ intermediate \rightarrow aminoaryl su				
arylamine	AM1	RM1	AM1	RM1			
aniline	-26.32	-39.23	-24.95	-30.63			
2-methylaniline	-22.32	-35.36	-27.40	-31.33			
3-methylaniline	-27.21	-40.71	-25.18	-30.44			
4-methylaniline	-23.53	-35.27	-24.92	-30.53			
2,6-dimethylaniline	-20.42	-34.63	-26.55	-31.91			
2-carboxyaniline (anthranilate anion)	-27.43	-38.11	-25.38	-30.54			
4-carboxyaniline (4-aminobenzoate anion)	-27.03	-38.56	-26.16	-31.95			
4-sulfoaniline (sulfanilate anion)	-36.67	-54.30	-26.09	-36.07			
4-sulfamoylaniline (sulfanilamide)	-37.41	-59.36	-29.85	-42.22			
4-phenylaniline	-24.89	-35.68	-25.70	-30.89			
4-bromoaniline	-31.48	-44.88	-26.23	-32.17			
3-chloroaniline	-29.66	-45.13	-26.41	-32.68			
2-nitroaniline	-37.19	-53.04	-26.66	-33.04			
N-methylaniline	-22.73	-35.86	-22.46	-24.25			
N-phenylaniline (diphenylamine)	-24.00	-36.31	-22.72	-25.30			



Figure 2. Reaction diagram of the Boyland-Sims oxidation of primary (R = H) and secondary (R = alkyl, aryl) arylamines.

Table 5. Ratio of Rate Constants $k_{C2(6)-O-SO_3}/k_{C4-O-SO_3}$ at T = 298 K in the Reaction of Nitrenium Cations of Aniline and Substituted Primary and Secondary Anilines with SO_4^{2-1} in an Alkaline Aqueous Solution, Computed by RM1/COS-MO Method

arylamine	$k_{\rm C2(6)-O}/k_{\rm C4-O}$ for ArNH ⁺ + SO ₄ ²⁻
aniline	3.93
2-methylaniline	4.42
3-methylaniline	C6 39.7
2-carboxyaniline (anthranilate anion	2.95
3-chloroaniline	C6 31.4
2-nitroaniline	25.6
N-methylaniline	1.72
N-phenylaniline (diphenylamine)	1.36

alkaline aqueous solution is analyzed (Table 7, Scheme 7). It is proved that N-C4 coupled diarylamines generally are prevalent products of oxidative dimerization of primary and secondary arylamines with S₂O₈²⁻, excepting 3-methylaniline and N-phenylaniline, which give N-C6 and C4-C4 coupled dimers, respectively. Arylamines substituted in para position are found to be N-C2(6) coupled (Table 7). It is interesting to note that the experimentally proved formation of arylamine dimers, e.g., 4-aminodiphenylamine (12, Scheme 5) in the case of aniline, in the oxidation of arylamines with $S_2O_8^2$ under acidic conditions,²⁷ has never been explained by the Behrman's mechanistic scheme. The arylhydroxylamine-O-sulfonates, proposed by Behrman as the key intermediates in the Boyland-Sims oxidation, have never been considered as possible intermediates in the mechanism of oxidative polymerization of aniline with $S_2O_8^{2-11-15,27,43-46}$. Arylamine dimers (12, Scheme 5) are further oxidized with $S_2O_8^{2-}$ to corresponding iminoquinonoid compounds.¹¹⁻¹⁵ The growth of oligoarylamine chain includes both the redox reactions of arylamines/oligoarylamines with oligomeric iminoquinonoid compounds, and electrophilic aromatic substitution reactions of arylamines/oligoarylamines with nitrenium cations of arylamines and fully oxidized oligoarylamines which have odd numbers of arylamine units. $^{11-15}$ The known experimental finding that there is a free-radical involvement in the formation of oligoarylamine precipitates during the Boyland–Sims oxidation, as judged by the inhibitory effects of allyl acetate and allyl alcohol,^{6a} is in excellent agreement with the recent quantum chemical finding that oxidations of arylamines with iminoquinonoid compounds include the formation of arylamine/oligoarylamine radical intermediate species.^{11,13,14}

The aminoaryl sulfates can be covalently incorporated into the oligoarylamine chains. The significant covalent inclusion of sulfur in oligoanilines precipitated during the early stages of the oxidative polymerization of aniline with $S_2 O_8^{2-}$ in water without added acid, which started in neutral/slightly alkaline reaction conditions and finished at pH <2, has been experimentally revealed by Trchová et al.³⁵ Manohar's group also proved the presence of residual sulfur in oligoaniline precipitates, obtained by the oxidation of aniline with $S_2O_8^{2-}$ in buffered aqueous solutions in the pH range 2.5–10.³⁹ The highest sulfur content in precipitated oligoanilines was determined at pH 4.5, while significantly decreased sulfur content was evidenced at pH 10. It was hypothesized that residual sulfur could originate from incomplete hydrolysis of aminoaryl sulfates formed as result of a Boyland-Sims type reaction.³⁹ The oxidative co-oligomerizations of arylamines with aminophenols, formed by hydrolysis of aminoaryl sulfates as well as by the reaction of arylnitrenium cations with both the OH⁻ in highly alkaline solution (11 \rightarrow 14, Scheme 5, Table 8) and water molecules in highly diluted aqueous solutions ($10 \rightarrow 13$, Scheme 5, Table 9), are also possible side oligomerization processes. It is computationally revealed that o-aminophenols are prevalent products of the reactions of arylnitrenium cations with OH⁻ (Table 8), with the exception of 2,6-dimethylaniline and N-methylaniline which prevalently give corresponding *p*-aminophenols. This reaction could be the main reason for the marked decrease of yield of aminoaryl sulfates with the increase of pH.⁷ The deprotonation of arylnitrenium cations to corresponding nitrenes (Scheme 2) under highly alkaline conditions, followed by the ring expansion to a 1,2-didehydroazepine,¹⁰ can also cause the decrease of yield of aminoaryl sulfates. In accordance with experimental findings,¹⁰ *p*-aminophenols are found to be prevalently formed in the reactions of arylnitrenium cations with H_2O (Table 9),

Table 6. Heats of Formation, $\Delta H_{\rm f}$ (kcal mol⁻¹), of the Intermediates [ArNR]OS₂O₇⁻ Formed in the Reaction of Nitrenium Cations of Aniline and Substituted Primary (R = H) and Secondary Anilines (R = Alkyl, Aryl) with S₂O₈²⁻ in an Alkaline Aqueous Solution, Computed by AM1/COSMO Method

		$\Delta H_{ m f}([m ArNR] m OS_2O_7^{-})~(m kcal~mol^{-1})$ by AM1/COSMO	
arylamine	N-O	C2(6)-O	C4-0
aniline	-378.34	-389.55	-388.29
2-methylaniline	-380.51	C6-394.24	-393.45
3-methylaniline	-384.53	C2-393.66	-391.46
		C6-395.78	
4-methylaniline	-385.79	-395.03	_
2,6-dimethylaniline	-382.61	_	-399.78
2-carboxyaniline (anthranilate anion)	-337.34^{a}	$C6 - 347.12^{a}$	-345.59^{a}
4-carboxyaniline (4-aminobenzoate anion)	-336.42^{a}	-342.06^{a}	_
4-sulfoaniline (sulfanilate anion)	-385.68^{a}	-394.58^{a}	_
4-sulfamoylaniline (sulfanilamide)	-336.86^{a}	-348.21^{a}	_
4-phenylaniline	-355.30	-363.63	_
4-bromoaniline	-374.58	-381.19	_
3-chloroaniline	-384.99	C2-391.89	-391.86
		C6-395.18	
2-nitroaniline	-256.33^{a}	$C6 - 270.61^{a}$	-269.64^{a}
N-methylaniline	-367.57	-386.55	-386.45
N-phenylaniline (diphenylamine)	-328.31	-355.44	-353.36
^a Computed by AM1 method in gas phase.			

Table 7. Heats of Formation, ΔH_f (kcal mol⁻¹), of the Intermediates [ArNR]ArNH⁺R Formed in the Reaction of Aniline and Substituted Primary (R = H) and Secondary Anilines (R = Alkyl, Aryl) with Their Nitrenium Cations ([ArNR]⁺ + ArNHR) in an Alkaline Aqueous Solution, Computed by AM1/COSMO Method

	$\Delta H_{\rm f}([{ m ArNR}]{ m ArNH}^+{ m R})~({ m kcal~mol}^{-1})$ by AM1/COSMO								
arylamine	N-N	N-C2(6)	N-C4	C2(6)-N	C2(6)-C2(6)	C2(6)-C4	C4-N	C4-C2(6)	C4-C4
aniline	183.31	161.88	159.93	177.65	176.00	173.33	174.93	176.49	171.72
2-methylaniline	172.57	C6 148.47	147.30	C6 162.17	C6-C6 165.17	C6 161.26	162.49	C6 165.78	160.20
3-methylaniline					C2-C2 165.29				
	1 (0 50	C2 148.56	1.15.10	C2 161.28	C2-C6 162.73	C2 160.54	1/1.05	C2 179.07	1/10/
	168.78	C6 144.98	145.42	C6 160.85	C6-C2 164.25	C6 160.69	161.95	C6 164.61	161.04
					C6-C6 161.52				
4-methylaniline	167.84	145.87	_	160.67	162.82	_	-	-	_
2,6-dimethylaniline	159.89	-	136.83	-	_	-	150.26	_	147.03
2-carboxyaniline (anthranilate)	-201.94	C6-222.58	-225.88	C6-206.56	C6-C6-207.53	C6-212.38	-207.61	C6-208.91	-215.02
4-carboxyaniline (4-aminobenzoate)	-204.64	-226.35	_	-210.79	-209.45	-	_	_	_
4-sulfoaniline (sulfanilate)	-322.64	-345.69	_	-327.27	-326.00	_	_	_	_
4-sulfamoylaniline (sulfanilamide)	-8.31	-33.47	_	-12.19	-10.78	-	_	_	_
4-phenylaniline	230.70	209.11	_	224.22	228.73	-	_	_	_
4-bromoaniline	193.81	170.57	_	187.74	188.73	-	_	_	_
3-chloroaniline					C2-C2 168.94				
	171 (0	C2 156.95	140.50	C2 165.56	C2-C6 166.54	C2 166.70	1/5 70	C2 181.84	1(4.24
	1/1.60	C6 149.95	148.59	C6 164.51	C6-C2 167.72	C6 164.54	165./8	C6 169.01	164.34
					C6-C6 166.37				
2-nitroaniline	189.53	C6 164.13	158.88	C6 177.35	C6-C6 175.12	C6 170.78	181.37	C6 177.18	172.34
N-methylaniline	204.25	178.26	176.37	190.74	186.87	181.89	188.17	185.29	179.06
N-phenylaniline (diphenylamine)	281.45	247.40	246.52	259.39	253.70	247.69	257.84	248.54	244.13

Scheme 7. Computationally Studied Intermediates in Reactions of Arylnitrenium Cations $[ArNR]^+$ with Parent Arylamines ArNHR: Aniline (R = R¹ = R² = R³ = R⁴ = H; 36 = 38, 39 = 47, 40 = 42 = 48 = 50, 41 = 49, 44 = 46) and Substituted Anilines (R = H, CH₃, C₆H₅; R¹ = H, CH₃, COO⁻, NO₂; R² = H, CH₃, Cl; R³ = H, CH₃, COO⁻, SO₃⁻, SO₂NH₂, C₆H₅, Br; R⁴ = H, CH₃), e.g., 3-Methylaniline (R = R¹ = R³ = R⁴ = H; R² = CH₃)



with the exception of 3-methylaniline, 2-nitroaniline, and parasubstituted anilines which prevalently give corresponding *o*aminophenols. Fully oxidized branched oligoarylamines, containing substituted phenazine and iminoquinonoid units, are proposed to be major component of insoluble precipitates.^{11,13,35,37,40–42} The presence of iminoquinone/phenoxazine segments in oligoarylamines, as a consequence of the incorporation of aminophenols, could be significant in highly alkaline and/or highly diluted aqueous solutions. The covalent inclusion of oxygen as well as the presence of iminoquinone segments in oligoanilines obtained by the oxidation of aniline with $S_2O_8^{\ 2-}$ at pH ≥ 2.5 was experimentally evidenced in several studies.^{38,39,47}

Our computational predictions of the key role of arylnitrenium cations in the formation of corresponding *o*-aminoaryl sulfates by the Boyland–Sims oxidation of primary and secondary arylamines raise the question of how tertiary arylamines, which can not form arylnitrenium cations, readily undergo Boyland-Sims oxidation. Tertiary arylamines, similarly to primary and secondary arylamines, were proved to be easily oxidized by the mild single-electron oxidants which cannot donate oxygen ([Fe(CN)₆]³⁻, +0.36 V vs NHE²⁵),⁴⁸ leading thus to the undisputable formation of corresponding cation radicals by single-electron transfer. It has also been unambiguously shown that tertiary arylamines, such as N,N-dimethylaniline (DMA), readily undergo sequential single-electron and twoelectron transfer reactions during the anodic oxidation,⁴⁹ leading to the formation of corresponding cation radicals and dications, respectively. The acid-base properties of the dications of tertiary arylamines have never been studied; i.e., the pK_{a} values of the dications of tertiary arylamines were not determined. However, the formation of immonium cations of tertiary arylamines (deprotonated forms of dications of tertiary arylamines) in alkaline solutions was proposed in several studies.⁵⁰ In the present study we provide semiempirical quantum chemical evidence that the Boyland-Sims oxidation of DMA^{1,8} (55, Scheme 8) leads to the initial formation of DMA dication (DMA^{2+}) (56, Scheme 8) and/ or DMA immonium cation (54, Scheme 8) by a two-electron transfer (rate-determining step), followed by the reaction between DMA^{2+}/DMA immonium cation and SO_4^{2-} within a solvent cage (regioselectivity-determining step); see Scheme 8.

Based on the modified Epiotis constraint,²⁸ our molecular orbital calculations have shown that DMA cation radical (DMA^{•+}) ($E_{\text{SOMO}} = -9.94 \text{ eV}$, $E_{\text{LUMO}} = -0.32 \text{ eV}$, RM1/COSMO), formed by single-electron oxidation of DMA with $S_2O_8^{2-}$ (reaction 10), can be easily oxidized further with generated $SO_4^{\bullet-}$ ($E_{\text{SOMO}} = -12.55 \text{ eV}$, $E_{\text{LUMO}} = +1.24 \text{ eV}$, RM1/COSMO) (reaction 11); i.e., $|E_{\text{SOMO}}(\text{DMA}^{\bullet+}) - E_{\text{LUMO}}(\text{SO}_4^{\bullet-})| < |E_{\text{SOMO}}(\text{SO}_4^{\bullet-}) - E_{\text{LUMO}}(\text{DMA}^{\bullet+})|$.

It follows that DMA oxidation in aqueous solution with $S_2O_8^{2-}$ does not stop after single-electron transfer (reaction 10) but proceeds further, i.e., leads to the DMA²⁺ in the initiation phase (reaction 11). It is open to discussion whether the formation of DMA²⁺ includes two sequential single-electron transfers (reactions 10 and 11), or DMA²⁺ is formed through concerted two-electron transfer (reaction 12).

$$C_{6}H_{5}N(CH_{3})_{2(aq)} + S_{2}O_{8}^{2^{-}}{}_{(aq)} \rightarrow [C_{6}H_{5}N(CH_{3})_{2}]^{\bullet^{+}}{}_{(aq)} + SO_{4}^{\bullet^{-}}{}_{(aq)} + SO_{4}^{2^{-}}{}_{(aq)}$$
(10)

$$[C_{6}H_{5}N(CH_{3})_{2}]^{\bullet+}{}_{(aq)} + SO_{4}^{\bullet-}{}_{(aq)} \rightarrow [C_{6}H_{5}N(CH_{3})_{2}]^{2+}{}_{(aq)} + SO_{4}^{2-}{}_{(aq)}$$
(11)

$$C_{6}H_{5}N(CH_{3})_{2(aq)} + S_{2}O_{8}^{2-}{}_{(aq)} \rightarrow [C_{6}H_{5}N(CH_{3})_{2}]^{2+}{}_{(aq)} + 2SO_{4}^{2-}{}_{(aq)}$$
(12)

We computed $\Delta H_{\rm f}$ values for ${\rm DMA}_{({\rm aq})}$ (25.67 kcal mol⁻¹, AM1/COSMO), ${\rm DMA}^{++}_{({\rm aq})}$ (156.98 kcal mol⁻¹, AM1/COSMO), and ${\rm DMA}^{2+}_{({\rm aq})}$ (307.58 kcal mol⁻¹, AM1/COSMO). On the basis of these data, accompanied by the computed data for $\Delta H_{\rm f}$ values for ${\rm S_2O_8^{2-}}_{({\rm aq})}$, ${\rm SO_4^{2-}}_{({\rm aq})}$, and ${\rm SO_4^{+-}}_{({\rm aq})}$, we calculated the heat of single-electron (reaction 10, $\Delta H_{\rm r}$ = +6.18 kcal mol⁻¹, AM1/COSMO) and two-electron (reaction 12, $\Delta H_{\rm r}$ = -13.4 kcal mol⁻¹, AM1/COSMO) redox reactions of DMA with ${\rm S_2O_8^{2-}}$ in aqueous solution. Thus we provide additional computational evidence that two-electron transfer in Boyland–Sims oxidation of DMA, leading to DMA^{2+},

Table 8. Heats of Formation, $\Delta H_f(\text{kcal mol}^{-1})$, of the Intermediates [ArNR]OH Formed in the Reaction of Nitrenium Cations of Aniline and Substituted Primary (R = H) and Secondary Anilines (R = Alkyl, Aryl) with OH⁻ in an Alkaline Aqueous Solution, Computed by AM1/COSMO Method

		$\Delta H_{ m f}([{ m ArNR}]{ m OH})~({ m kcal~mol}^{-1})$ by AM1/COSMO	
arylamine	N-O	C2(6)—O	C4-0
aniline	2.54	-12.03	-10.84
2-methylaniline	-4.64	C6-18.34	-16.92
3-methylaniline	-5.07	C2-19.09	-17.68
		C6-20.15	
4-methylaniline	-5.16	-19.93	_
2,6-dimethylaniline	-6.33	_	-24.39
2-carboxyaniline (anthranilate anion)	-189.83	C6-205.88	-205.41
4-carboxyaniline (4-aminobenzoate anion)	-189.48	-206.89	_
4-sulfoaniline (sulfanilate anion)	-252.83	-266.17	_
4-sulfamoylaniline (sulfanilamide)	-96.86	-105.95	_
4-phenylaniline	25.54	11.38	_
4-bromoaniline	6.29	-7.67	_
3-chloroaniline	-4.56	C2-17.56	-15.94
		C6-18.69	
2-nitroaniline	-0.56	C6-16.43	-12.61
<i>N</i> -methylaniline	10.09	-9.80	-10.11
N-phenylaniline (diphenylamine)	45.60	20.18	20.29

Table 9. Heats of Formation, $\Delta H_{\rm f}$ (kcal mol⁻¹), of the Intermediates [ArNR]OH₂⁺ Formed in the Reaction of Nitrenium Cations of Aniline and Substituted Primary (R = H) and Secondary Anilines (R = Alkyl, Aryl) with H₂O in an Alkaline Aqueous Solution, Computed by AM1/COSMO Method

	$\Delta H_{ m f}([{ m ArNR}]{ m OH_2}^+)~({ m kcal~mol}^{-1})$ by AM1/COSMO				
arylamine	N-O	C2(6)—O	C4-0		
aniline	139.50	115.50	114.52		
2-methylaniline	131.99	C6 109.47	108.84		
3-methylaniline	131.42	C2 111.50	108.30		
		C6 107.82			
4-methylaniline	131.04	107.73	_		
2,6-dimethylaniline	126.47	_	102.01		
2-carboxyaniline (anthranilate anion)	-55.56	C6-78.48	-78.82		
4-carboxyaniline (4-aminobenzoate anion)	-55.61	-78.67	_		
4-sulfoaniline (sulfanilate anion)	-114.42	-133.11	_		
4-sulfamoylaniline (sulfanilamide)	42.34	22.53	_		
4-phenylaniline	162.53	140.02	_		
4-bromoaniline	142.52	121.97	_		
3-chloroaniline	131.11	C2 113.61	111.96		
		C6 112.01			
2-nitroaniline	137.74	C6 114.67	117.57		
<i>N</i> -methylaniline	147.18	116.19	115.16		
N-phenylaniline (diphenylamine)	180.81	148.29	146.25		

is thermodynamically more favorable than single-electron transfer leading to DMA^{•+}.

Since the kinetics of deprotonation of DMA^{2+} is undetermined, it is open to discussion whether DMA^{2+} or DMA immonium cation will react further in a regioselectivity-determining step with SO_4^{2-} which is simultaneously formed within the same solvent cage. The positive charge distribution on both DMA²⁺ (**56**) and DMA immonium cation (**54**), represented by their resonance hybrids (Scheme 8), indicates that N, C2(6), and C4 are the main DMA²⁺/DMA immonium cation reactive centers.

The regioselectivity of the coupling reactions of DMA^{2+} and DMA immonium cation with SO_4^{2-} is governed by the stability of intermediates (51–53 and 57–59, Scheme 8) resembling structurally the corresponding transition states. In accordance with Boyland and Sims experiments,¹ it is proved by both AM1 and RM1 methods (Table 10) that the most stable intermediates (52 and 58) are formed by the C2(6)–O–SO₃⁻ couplings in

Scheme 8. Boyland-Sims Oxidation of *N*,*N*-Dimethylaniline: Formation of Possible Intermediates



the reaction of DMA^{2+} with SO_4^{2-} as well as in the reaction of DMA immonium cation with SO_4^{2-} .

CONCLUSIONS

In summary, a revised mechanism of the Boyland-Sims oxidation of arylamines, based on the unique role of arylnitrenium cations in the case of primary and secondary arylamines, and arylamine dications and/or immonium cations in the case of tertiary arylamines, comprehensively explained the formation of soluble aminoaryl sulfates and insoluble oligoarylamines more consistently with experimental evidence than previous mechanistic schemes. It was revealed that the two-electron transfer between arylamine and peroxydisulfate, accompanied by deprotonation, leading to the formation of arylnitrenium cations/ arylamine dications/immonium cations and sulfate anions, represents a rate-determining step, while the subsequent reaction between arylnitrenium cations/arylamine dications/immonium cations and sulfate anions represents a regioselectivity-determining step. In accordance with Boyland's and Sims's experimental findings, the reactions of arylnitrenium cations and arylamine dications/immonium cations with sulfate anions, formed by the oxidation of arylamines with peroxydisulfate, are proved by both the AM1 and RM1 semiempirical quantum chemical methods to lead to the prevalent formation of o-aminoaryl sulfates. C6- $O-SO_3^-$ rather than $C2-O-SO_3^-$ coupled aminoaryl sulfates are computationally confirmed to be major products in the case of meta-substituted anilines which have unsymmetrical ortho positions. If both ortho positions are blocked by substituents, calculations confirmed known experimental findings that para substitution occurs. The reactions between arylnitrenium cations and peroxydisulfate in an aqueous solution were found to have regioselectivities quite similar to those of the reactions between arylnitrenium cations and sulfate; i.e., they lead to the prevalent formation of o-aminoaryl peroxydisulfates, which undergo rapid reduction to the corresponding o-aminoaryl sulfates. The formation of insoluble precipitates during the Boyland-Sims oxidation of arylamines is due to the oxidative oligomerization of arylamines, in which the dimerization phase is the reaction of arylamine with its reactive species generated by two-electron transfer. The oxidative co-oligomerizations of arylamines with aminoaryl sulfates and aminophenols, formed by the reaction of arylnitrenium cations/arylamine dications/immonium cations with both hydroxide anions in highly alkaline solution and water molecules in highly diluted aqueous solutions, are proposed to be side reactions. Fully oxidized branched oligoarylamines, containing mainly substituted phenazine and iminoquinonoid units, with the presence of iminoquinone/phenoxazine segments, are proposed to constitute insoluble precipitates.

Table 10. Heats of Formation, ΔH_f (kcal mol⁻¹), of the Intermediates $[C_6H_5N^+(CH_3)_2]OSO_3^-$ and $[C_6H_5N^+CH_2^-(CH_3)]OSO_3^-$ Formed in Reactions of SO_4^{2-} with *N*,*N*-Dimethylaniline Dication and Immonium Cation, Respectively, Computed by AM1 and RM1 Methods

	$\Delta H_{ m f}(m kcalmol^{-1})$						
		AM1			RM1		
intermediate	N-O	C2(6)-O	C4-0	N-O	C2(6)-O	C4-0	
$[C_6H_5N^+(CH_3)_2]OSO_3^-$ $[C_6H_5N^+CH_2^-(CH_3)]OSO_3^-$	-74.61 -81.43	-100.58 -145.15	-91.81 -139.81	-93.50 -109.11	-112.83 -163.01	-105.02 -158.87	

The present contribution not only gives new insights into the mechanism of Boyland–Sims oxidation, but also opens up new opportunities for scientists working in the field of conducting poly(aromatic amines) to elucidate the molecular structures of oligoarylamines, e.g., oligoanilines. This is especially important because oligoanilines serve as templates in the synthesis of polyaniline nanotubes, nanorods, and nanosheets, by the oxidative polymerization of aniline with ammonium peroxydisulfate under decreasing pH conditions (start in alkaline/slightly acidic solutions and finish at pH <2.0). A revised mechanism of the Boyland–Sims oxidation indicates the incorporation of both aminophenols and aminoaryl sulfates into the oligoaniline precipitates.

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