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COMMENT
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Reply to "Comment on 'Revised Mechanism of Boyland−Sims Oxidation'"

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Recently, we reported the new computational insights into the mechanism of Boyland−Sims oxidation of arylamines with peroxydisulfate ($S_2O_8^{2-}$) in an alkaline aqueous solution.[1] The classic Behrman's mechanism[2] has been revised; i.e., we proposed 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, based on the AM1 and RM1 semiempirical quantum chemical study of the Boyland−Sims oxidations of aniline, 12 ring-substituted and 3 *N*-substituted anilines, which were experimentally studied by Boyland and Sims more than five decades ago.[3] Quantum chemical results indicate that arylnitrenium cations and sulfate anions (SO_4^{2-}) are generated by the 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 $S_2O_8^{2-}$. For the first time the regioselectivity of Boyland−Sims oxidation was explained. It was computationally found that the regioselectivity-determining reaction of arylnitrenium cations/arylamine dications/immonium cations and SO_4^{2-}, within the solvent cage, leads to the prevalent formation of *o*-aminoaryl sulfates. The formation of insoluble oligomeric/polymeric precipitates during the Boyland−Sims oxidation of arylamines was also computationally studied. We proposed that the reaction between arylamine and its nitrenium cation, whenever the formation of *p*-/*o*-iminoquinonoid product is not possible, represents dimerization route in the oxidative oligomerization of primary and secondary arylamines with $S_2O_8^{2-}$ which generally leads to the formation of N−C4 coupled arylamine dimers. The oxidative co-oligomerizations of arylamines with more oxidizable aminoaryl sulfates and aminophenols,[4] formed by the reaction of arylnitrenium cations/arylamine dications/immonium cations with the hydroxide anions in highly alkaline solution and with water molecules in highly diluted aqueous solutions, are proposed to lead to insoluble precipitates.[1,4]

In the foregoing Comment,[5] Behrman made some comments and observations on our computational study of the mechanism of Boyland−Sims oxidation.[1] Behrman's starting statements[5] "*Peroxydisulfate ions react with aromatic amines in two ways depending on whether the amine is protonated or not. Under alkaline conditions, o-aminoarylsulfates are formed. This is the Boyland−Sims oxidation. Under acidic conditions, these sulfates are not formed but rather the amines are polymerized to form polyanilines*" simplified the present state of the art of both the Boyland−Sims oxidation and oxidative polymerization of arylamines. It is well-known that the Boyland−Sims oxidation of arylamines can be efficiently carried out in a broad pH range from highly alkaline to slightly acidic conditions because of the prevalence of reactive species $ArNH_2$ at pH > 5 (pK_a $ArNH_3^+/ArNH_2$ of the most of arylamines is <5). The formation of *o*-aminophenylsulfate even under more acidic conditions (pH ≥ 2.5) is proposed in a recent study done by Surwade et al.,[6] to explain the evidenced covalent inclusion of sulfur in oligoaniline precipitates formed by the oxidation of aniline with $S_2O_8^{2-}$ in buffered aqueous solutions in the pH range 2.5−10. The determination of pH limit for the formation of aminoarylsulfates under acidic conditions thus remains a challenge. On the other hand, it is also well documented that the polymerization of aniline was not only performed under acidic conditions but also can be started under alkaline/neutral/slightly acidic conditions and finished in highly acidic media (pH ≤ 2) by using so-called "falling-pH method".[7] It seems that simultaneous formation of soluble aminoarylsulfates and insoluble oligo/polyarylamines occur in a very broad pH range.

Behrman's interpretation of our mechanistic concept in his comment[5] "*Marjanović et al.[1] have proposed that a nitrenium ion is formed in the rate-determining step as the first intermediate at all pH values*", is not in accordance with our statement[1] "Acid−base properties of aniline nitrenium cation[10] 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 presence of non-oxidizable acids/salts (sulfuric acid/sulfates/hydrogen sulfates, etc.).". The difference between "*all pH values*" and "very broad pH range" is fundamental for understanding our mechanistic concept because the reactivity of arylnitrenium cations is quite different in comparison with the reactivity of corresponding arylnitrenes and arylamine dications.[8] For example, we suggested[1] that the deprotonation of arylnitrenium cations to corresponding arylnitrenes, followed by the ring expansion to a 1,2-didehydroazepines,[8] is one of possible reasons for the observed decrease of yield of aminoaryl sulfates under highly alkaline conditions (pH > 13).

Behrman's interpretation[5] of our computational results "*Their proposal is based on calculations which show that the ion pair of the nitrenium ion (formed from 75 different aryl amines) and sulfate has*

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a lower heat of formation than the corresponding arylhydroxylamine-O-sulfonate" is also not consistent with our results and discussion.[1] Our proposal[1] that arylnitrenium cations and 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 $S_2O_8^{2-}$, is based on quantum chemical results that arylamine radical species formed by single-electron oxidation of arylamines with powerful oxidant $S_2O_8^{2-}$ (2.0−2.1 V vs NHE)[9] can be readily further oxidized with $SO_4^{\bullet-}$ (product of peroxydisulfate single-electron reduction), which is a stronger oxidant (2.5−3.1 V vs NHE)[10] compared with $S_2O_8^{2-}$. We also provide quantum chemical evidence that two-electron oxidation in Boyland−Sims oxidation of arylamines is generally thermodynamically more favorable than single-electron oxidation. As a minor correction of Behrman's statement mentioned above, it should also be noted that we have computationally studied the formation of arylnitrenium cations not from 75 but from 15 different arylamines (aniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 2,6-dimethylaniline, anthranilic acid, 4-aminobenzoic acid, sulfanilic acid, sulfanilamide, 4-phenylaniline, 4-bromoaniline, 3-chloroaniline, 2-nitroaniline, *N*-methylaniline, and diphenylamine).[1]

Behrman's observation[5] "*In support of a duality of routes, I point out that the formation of a nitrenium ion might be favored under acidic conditions because no charge separation is involved in contrast to the formation of a nitrenium ion from an uncharged amine*" is not consistent with the known fact that arylamines are much more susceptible to the anodic electron transfer oxidations under alkaline conditions, when they are nonprotonated, than under acidic conditions when they exist prevalently in protonated form.[11]

Behrman's statement[5] "*To arrive at the intermediate shown in ref 1, Figure 2 (a nitrenium ion and two sulfates), the transition state must involve the formation of a transient hydride ion (or an electron pair) which then attacks one of the peroxide oxygens, leading to heterolytic cleavage of the peroxide bond. This seems an unlikely process on the basis of electronegativity values*", regarding the initial electron transfer between arylamine and $S_2O_8^{2-}$, is disputable. We pointed out[1] "It is open to discussion whether the formation of arylnitrenium cations include two sequential single-electron transfers and well-defined deprotonation steps (e.g., in alkaline solutions of aniline, **C** → **D** → **E** → **G**, or **C** → **D** → **F** → **G**, Scheme 2), or arylnitrenium cations are formed through concerted two-electron transfer accompanied with deprotonation. Radical trap experiments[6a] indicate that concerted mechanism is more probable." It is evident that the mechanism of quite complex initial electron transfer between arylamine and $S_2O_8^{2-}$, accompanied with deprotonation, is not a closed case for us, on contrary, it remains a challenge. Several different two-electron transfer mechanisms, which lead to the formation of solvated tight ion pair $[ArNR]^+/SO_4^{2-}$, are possible, e.g.,

(a) Sequential reactions 1, 2, and 3

$$\mathrm{ArNHR} + \mathrm{S_2O_8}^{2-} \rightarrow ([\mathrm{ArNHR}]^{\bullet+} + \mathrm{SO_4}^{\bullet-})_{\text{radical pair}} + \mathrm{SO_4}^{2-} \tag{1}$$

$$([\mathrm{ArNHR}]^{\bullet+} + \mathrm{SO_4}^{\bullet-})_{\text{radical pair}} + \mathrm{SO_4}^{2-} \rightarrow ([\mathrm{ArNHR}]^{2+} + \mathrm{SO_4}^{2-})_{\text{ion pair}} + \mathrm{SO_4}^{2-} \tag{2}$$

$$([\mathrm{ArNHR}]^{2+} + \mathrm{SO_4}^{2-})_{\text{ion pair}} + \mathrm{SO_4}^{2-} \rightarrow ([\mathrm{ArNR}]^{+} + \mathrm{SO_4}^{2-})_{\text{ion pair}} + \mathrm{SO_4}^{2-} + \mathrm{H}^+ \tag{3}$$

(b) Concerted reactions 1 and 2, followed by reaction 3
(c) Reaction 1, followed by the concerted reactions 2 and 3
(d) Sequential reactions 1, 4, and 5

$$([\mathrm{ArNHR}]^{\bullet+} + \mathrm{SO_4}^{\bullet-})_{\text{radical pair}} + \mathrm{SO_4}^{2-} \rightarrow ([\mathrm{ArNR}]^{\bullet} + \mathrm{SO_4}^{\bullet-})_{\text{radical pair}} + \mathrm{SO_4}^{2-} + \mathrm{H}^+ \tag{4}$$

$$([\mathrm{ArNR}]^{\bullet} + \mathrm{SO_4}^{\bullet-})_{\text{radical pair}} + \mathrm{SO_4}^{2-} + \mathrm{H}^+ \rightarrow ([\mathrm{ArNR}]^{+} + \mathrm{SO_4}^{2-})\text{ion pair} + \mathrm{SO_4}^{2-} + \mathrm{H}^+ \tag{5}$$

(e) Concerted reactions 1 and 4, followed by reaction 5

Numerous additional questions, e.g., whether mentioned electron transfers represent inner-sphere or outer-sphere electron transfer processes, still remain to be answered.

Behrman's comment[5] "*The other product of the peroxydisulfate oxidation of aromatic amines under alkaline conditions is a brown humic acid-like material with IR and electronic spectra quite distinct from those of the violet-blue or green polyanilines.[7−9] Marjanović et al.[1] appear to regard these two materials as the same*" is not consistent with the fact that there is no single sentence in our paper that indicates we regard brown humic acid-like oligomeric precipitates, formed by the oxidation of arylamines with $S_2O_8^{2-}$ at pH ≥ 2.5, and polyarylamine precipitates formed by the oxidation of arylamines with $S_2O_8^{2-}$ in acidic media at pH ≤ 2, which have different colors depending on oxidation state and protonation degree, as the same. It has been proved by several research groups[6,12] that nonconducting aniline oligomers formed by the oxidation of aniline with $S_2O_8^{2-}$ at pH ≥ 2.5 have a quite different structure in comparison with conducting polyaniline formed by the oxidation of aniline with $S_2O_8^{2-}$ in acidic media at pH ≤ 2. Recent computational study done by Ćirić-Marjanović et al.[13] indicated that linear N−C4 coupled aniline oligomers in pernigraniline salt form, which can efficiently propagate the growth of conducting polyaniline, are prevalently formed by the oxidation of aniline with $S_2O_8^{2-}$ only at pH ≤ 2. We suggested[1,4] that fully oxidized branched oligoarylamines containing substituted phenazines, iminoquinonoid units, iminoquinone/phenoxazine segments, and aminoaryl sulfate units, constitute insoluble precipitates formed by the oxidation of arylamines with $S_2O_8^{2-}$ at pH ≥ 2.5. According to our mechanistic concept, the major difference between the mechanism of oxidative oligomerization of arylamines with $S_2O_8^{2-}$ at pH ≥ 2.5 and corresponding oxidative polymerization at pH ≤ 2 is not the initiation and dimerization phase, but the propagation phase.

Regarding Behrman's observations[5] "*They also argue that because molecules such as 4-aminodiphenylamine and benzidine do not undergo the Boyland−Sims oxidation, the displacement mechanism is wrong, but several 4-aminodiphenyls and diphenylamine are on record as behaving normally in this reaction. A complex radical mechanism is involved in the oxidation of N,N-dimethyl-p-phenylenediamine*", it should be stressed that all 4-aminodiphenyls and diphenylamine, which behave normally in Boyland−Sims oxidation,[14] cannot form stable iminoquinonoid compounds upon the two-electron oxidation; i.e., the products of their initial two-electron oxidation have arylnitrenium cation character. The products of the two-electron oxidation of benzidine, 4-aminodiphenylamine, *N*,*N*-dimethyl-*p*-phenylenediamine and similar compounds with $S_2O_8^{2-}$ are not arylnitrenium cations but iminoquinonoid compounds that cannot react with SO_4^{2-}. These iminoquinonoid compounds are oxidants and, depending on the reaction conditions, e.g., presence of reductants, can further undergo redox processes.[15]

Behrman's thinking that the kinetic barrier to the formation of arylamine dications from unprotonated tertiary arylamines, which cannot form iminoquinonoid compounds upon the two-electron oxidation, would be formidable[5] is not supported by our quantum chemical results[1] as well as by the electrochemical experiments.[16]

The fact that allyl acetate, a well-known radical trap reagent, has no effect on the yield of 2-aminopyridine-3-sulfate from 2-aminopyridine under alkaline conditions led Behrman more than four decades ago to the correct conclusion that there is no involvement of free radical species in the mechanism of the formation of aminoaryl sulfates by Boyland−Sims oxidation.[2] Now Behrman suggests in his Comment,[5] based on the reaction between acylarylnitrenium cation and electron-rich alkenes,[17] that allyl acetate can also be an arylnitrenium cation trap reagent in Boyland−Sims oxidation. We disagree with this suggestion because (a) allyl acetate is not an electron-rich alkene and (b) the rate constant of the tentative reaction between arylnitrenium cations and allyl acetate should be significantly higher in comparison with the rate constants of the reactions between arylnitrenium cations and electron-rich reactive species already present in reaction media (SO_4^{2-}, arylamine, OH^-) for efficient trapping of the arylnitrenium cations with allyl acetate. Therefore, it can be concluded that the absence of the inhibiting effect of allyl acetate on either the rate or extent of aminoaryl sulfate formation under alkaline conditions[2] do not represent proof or indication against the arylnitrenium cation involvement in aminoaryl sulfate formation but only the experimental proof against the free radical species involvement. The fact that allyl acetate inhibits the oxidative polymerization of aniline by $S_2O_8^{2-}$ in acidic solutions[18] is not a consequence of the inhibition of initiation and dimerization phase of polymerization via the arylnitrenium cation trapping, but it is a consequence of the inhibition of propagation phase which is known to include free radical species.[13]

Finally, aware that the regioselectivity in the formation of aminoaryl sulfates was well explained by the involvement of arylnitrenium cations in the mechanism of Boyland−Sims oxidation,[1] Behrman offered in the last paragraph of his Comment[5] the modified classic mechanism of Boyland−Sims oxidation with involvement of arylnitrenium cations: "*first formation of the arylhydroxylamine-O-sulfonate by displacement in the rate-determining step followed by rearrangement to the nitrenium ion*" (reactions 6 and 7).

$$\mathrm{ArNHR} + \mathrm{S_2O_8^{2-}} \rightarrow \mathrm{Ar(R)NH^+OSO_3^-} + \mathrm{SO_4^{2-}} \qquad (6)$$

$$\mathrm{Ar(R)NH^+OSO_3^-} + \mathrm{SO_4^{2-}} \rightarrow ([\mathrm{ArNR}]^+ + \mathrm{SO_4^{2-}})\text{ion pair} + \mathrm{SO_4^{2-}} + \mathrm{H^+} \qquad (7)$$

This modified classic Behrman's mechanism of Boyland−Sims oxidation, which changes the focus from the question whether or not arylnitrenium cations are formed during the Boyland−Sims oxidation to the question how arylnitrenium cations are formed, cannot simply be ruled out. Besides the already mentioned reasons in our article[1] in favor of the initial two-electron transfer process and against the S_N2 nucleophilic displacement by the arylamine nitrogen on peroxide oxygen of $S_2O_8^{2-}$, we here provide some additional arguments. In both proposed electron transfer and S_N2 nucleophilic displacement processes the initial reaction between arylamine and $S_2O_8^{2-}$ is governed by the $\mathrm{HOMO_{arylamine}}-\mathrm{LUMO_{peroxydisulfate}}$ interaction. The S_N2 nucleophilic displacement by the aniline nitrogen on peroxide oxygen of $S_2O_8^{2-}$ will be potentially favorable only in the case of pronounced localization of aniline HOMO on nitrogen atom and peroxydisulfate LUMO on peroxide oxygen. On the other hand, the electron transfer process will be favorable in the case of delocalized aniline HOMO and peroxydisulfate LUMO. Our computations of aniline HOMO, which are in agreement with literature data,[19] show that the aniline HOMO is a delocalized π−orbital whose p-lobes are centered on the C1, C4, and N atoms (Figure 1). Our computations also show that peroxydisulfate LUMO is highly delocalized orbital (Figure 2). It follows that HOMO−LUMO computations do not support S_N2 nucleophilic displacement but electron transfer.

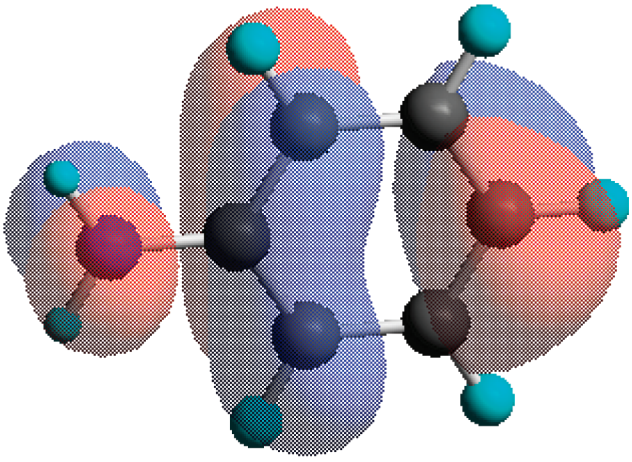

Figure 1. Aniline HOMO computed by AM1/COSMO.

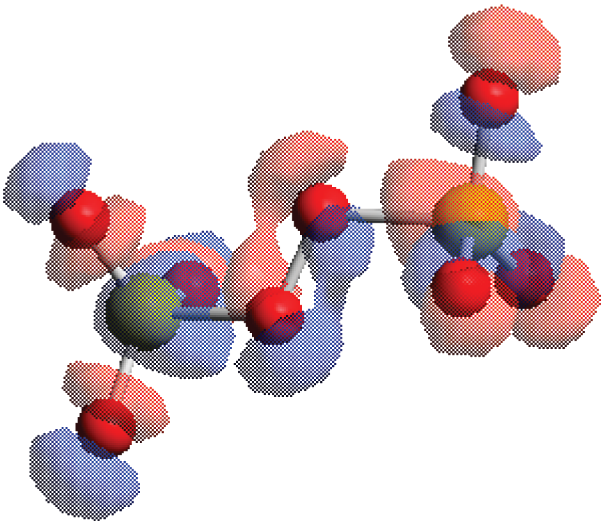

Figure 2. Peroxydisulfate dianion LUMO computed by AM1/COSMO.

It should also be noted that the S_N2 nucleophilic displacement by any nucleophile on peroxide oxygen of $S_2O_8^{2-}$ is disputable since the peroxide O—O bond in $S_2O_8^{2-}$ is nonpolar with a negative Mulliken charges of −0.65 on both peroxide oxygen atoms, as determined by our AM1/COSMO computations.

It can be concluded that the past work devoted to the oxidation of arylamines with $S_2O_8^{2-}$ done by conducting polymer scientists, which were focused on the structure and properties of formed oligo/polyarylamine precipitates, as well as the past work of chemists focused on the formation of soluble aminoaryl sulfates, was somewhat misleading regarding the mechanism of oxidation of arylamines with $S_2O_8^{2-}$. Only collaborative work of scientists from both fields with comprehensive approach to the study of insoluble as well as soluble products can bring the new light into the mechanism of oxidation of arylamines with $S_2O_8^{2-}$.

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