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 peroxysulfate (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2—}) in an alkaline aqueous solution.\textsuperscript{1} The classic Behrman’s mechanism\textsuperscript{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 ions, in the case of tertiary arylamines, in the formation of corresponding o-aminaryl 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.\textsuperscript{3} Quantum chemical results indicate that arylnitrenium cations and sulfate ions (SO\textsubscript{4}\textsuperscript{2—}) are generated by the rate-determining two-electron oxidation of primary and secondary arylamines with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2—}, while arylamine dications/immonium ions and SO\textsubscript{4}\textsuperscript{2—} are initially formed by two-electron oxidation of tertiary arylamines with S\textsubscript{2}O\textsubscript{8}\textsuperscript{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 ions and SO\textsubscript{4}\textsuperscript{2—}, within the solvent cage, leads to the prevalent formation of o-aminaryl 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-inoquinonoid product is not possible, represents dimerization route in the oxidative oligomerization of primary and secondary arylamines with S\textsubscript{2}O\textsubscript{8}\textsuperscript{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,\textsuperscript{4} formed by the reaction of arylnitrenium cations/arylamine dications/immonium ions with the hydroxide anions in highly alkaline solution and with water molecules in highly diluted aqueous solutions, are proposed to lead to insoluble precipitates.\textsuperscript{1,4}

In the foregoing Comment,\textsuperscript{5} Behrman made some comments and observations on our computational study of the mechanism of Boyland—Sims oxidation.\textsuperscript{1} Behrman’s starting statements “Peroxysulfate ions react with aromatic amines in two ways depending on whether the amine is protonated or not. Under alkaline conditions, o-aminaryl sulfates are formed. This is the Boyland—Sims oxidation. Under acidic conditions, these sulfates are not formed but rather the amines are polymerized to form polyarylimes” 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\textsubscript{2} at pH > 5 (pK\textsubscript{a} ArNH\textsubscript{2}/ArNH\textsubscript{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.,\textsuperscript{6} to explain the evidenced covalent inclusion of sulfur in oligoaniline precipitates formed by the oxidation of aniline with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2—} in buffered aqueous solutions in the pH range 2.5—10. The determination of pH limit for the formation of aminoaaryl sulfates 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”.\textsuperscript{7}

Behrman’s interpretation of our mechanistic concept in his comment\textsuperscript{5} Marjanović et al.\textsuperscript{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 “Acid—base properties of aniline nitrenium cation\textsuperscript{10} indicate that it is a very weak acid in water, pK\textsubscript{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\textsubscript{a} > 13.0. It can be concluded that the generation of aniline nitrenium cation is the common feature of all known aniline oxidations with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2—} in the very broad pH range, in the presence of non-oxidizable acids/salts (sulfuric acid/sulfates/hydrogen sulfates, etc.).\textsuperscript{8} 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.\textsuperscript{8} For example, we suggested\textsuperscript{1} that the deprotonation of arylnitrenium cations to corresponding arylnitrenes, followed by the ring expansion to a 1,2-dihydropyridines,\textsuperscript{8} is one of possible reasons for the observed decrease of yield of aminoaryl sulfates under highly alkaline conditions (pH > 13).

Behrman’s interpretation\textsuperscript{5} of our computational results “Their proposal is based on calculations which show that the ion pair of the nitrenium ion (formed from 7S 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 proposal1 that aryltriminium cations and SO$_{4}^{2-}$ are generated by
rate-determining two-electron oxidation of primary and
secondary arylamines with S$_2$O$_8^{2-}$, while arylamine dications/
immonium cations and SO$_{4}^{2-}$ are initially formed by two-
electron oxidation of tertiary arylamines with S$_2$O$_8^{2-}$, is based on
quantum chemical results that arylamine radical species
formed by single-electron oxidation of arylamines with powerful
oxidant S$_2$O$_8^{2-}$ (2.0–2.1 V vs NHE)$^9$ can be readily further
oxidized with SO$_4^{2-}$ (product of peroxisulfate single-electron
reduction), which is a stronger oxidant (2.5–3.1 V vs NHE)$^9$
compared with S$_2$O$_8^{2-}$. 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 aryltriminium
cations not from 75 but from 15 different arylamines (aniline,
2-methylaniline, 3-methylaniline, 4-methylaniline, 2,6-dimethy-
laniline, antranilic 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$_2$O$_8^{2-}$, is disputable.
We pointed out$^7$ “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 $\rightarrow$ D $\rightarrow$ E $\rightarrow$ G, or C $\rightarrow$ D $\rightarrow$ F $\rightarrow$ G,
Scheme 2), or aryltriminium cations are formed through concerted
two-electron transfer accompanied with deprotonation.
Radical trap experiments$^{13,14}$ indicate that concerted mechanism
is more probable.” It is evident that the mechanism of quite
complex initial electron transfer between arylamine and S$_2$O$_8^{2-}$,
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 [ArNHR]$^+$/SO$_4^{2-}$, are possible, e.g.,
(a) Sequential reactions 1, 2 and 3

\[
\text{ArNHR} + S_2O_8^{2-} \rightarrow ([\text{ArNHR}]^+ + \text{SO}_4^{2-})_{\text{radical pair}} + \text{SO}_4^{2-}
\]  \hspace{1cm} (1)

\[
([\text{ArNHR}]^+ + \text{SO}_4^{2-})_{\text{radical pair}} + \text{SO}_4^{2-}
\]

\[
\rightarrow ([\text{ArNHR}]^{2+} + \text{SO}_4^{2-})_{\text{ion pair}} + \text{SO}_4^{2-}
\]  \hspace{1cm} (2)

\[
([\text{ArNHR}]^{2+} + \text{SO}_4^{2-})_{\text{ion pair}} + \text{SO}_4^{2-} \rightarrow ([\text{ArNHR}]^{+} + \text{SO}_4^{2-})_{\text{ion pair}} + \text{SO}_4^{2-} + \text{H}^+
\]

\[\rightarrow ([\text{ArNHR}]^{+} + \text{SO}_4^{2-})_{\text{ion pair}} \]  \hspace{1cm} (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

\[
([\text{ArNHR}]^{+} + \text{SO}_4^{2-})_{\text{radical pair}} + \text{SO}_4^{2-} \rightarrow ([\text{ArNHR}]^{+} + \text{SO}_4^{2-})_{\text{ion pair}} + \text{SO}_4^{2-} + \text{H}^+
\]

\[\rightarrow ([\text{ArNHR}]^{+} + \text{SO}_4^{2-})_{\text{ion pair}} \]  \hspace{1cm} (4)

(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.10 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$_2$O$_8^{2-}$
at pH $\geq$ 2.5, and polyanilamine precipitates formed by the
oxidation of arylamines with S$_2$O$_8^{2-}$ in acidic media at pH $\leq$ 2,
which have different colors depending on oxidation state and
protonation degree, as the same. It has been proved by several
research groups$^8,12$ that nonconducting aniline oligomers formed
by the oxidation of aniline with S$_2$O$_8^{2-}$ at pH $\geq$ 2.5 have a quite
different structure in comparison with conducting polyanilines
formed by the oxidation of aniline with S$_2$O$_8^{2-}$ in acidic media at
pH $\leq$ 2. Recent computational study done by Cirić-Marjanović
et al.$^{10}$ indicated that linear N–C4 coupled aniline oligomers in
pernigraniline salt form, which can efficiently propagate the
growth of conducting polyanilines, are prevalently formed by
the oxidation of aniline with S$_2$O$_8^{2-}$ only at pH $\leq$ 2. We
suggested$^{14,15}$ that fully oxidized branched oligoarylamines con-
taining substituted phenazines, iminoquinonoid units, iminoqui-
none/phenoxazine segments, and aminooaryl sulfite units,
constitute insoluble precipitates formed by the oxidation of
arylamines with S$_2$O$_8^{2-}$ at pH $\geq$ 2.5. According to our mechan-
istic concept, the major difference between the mechanism of
oxidative oligomerization of arylamines with S$_2$O$_8^{2-}$ at pH $\geq$ 2.5
and corresponding oxidative polymerization at pH $\leq$ 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 mechan-
ism 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-phenyle-
nediamine”, 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 \( \text{S}_2\text{O}_8^{2-} \) are not arylnitrenium cations but iminoquinonoid compounds that cannot react with \( \text{SO}_4^{2-} \). These iminoquinonoid compounds are oxidants and, depending on the reaction conditions, e.g., presence of reductants, can further undergo redox processes.\(^5\)

Behrmann’s thinking that the kinetic barrier to the formation of arylnitrenium 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\(^4\) as well as by the electrochemical experiments.\(^6\)

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 Behrmann 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 Behrmann suggests in his Comment,\(^5\) based on the reaction between acylaryl nitrenium cation and electron-rich alkenes,\(^17\) that allyl acetate can also be an aryl nitrenium 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 (\( \text{SO}_4^{2-} \), arylamine, \( \text{OH}^- \)) 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\(^5\) 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 \( \text{S}_2\text{O}_8^{2-} \) 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,\(^1\) Behrmann 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).

\[
\text{ArNHR + S}_2\text{O}_8^{2-} \rightarrow \text{Ar(R)NH}^+\text{OSO}_3^- + \text{SO}_4^{2-} \quad (6)
\]

\[
\text{Ar(R)NH}^+\text{OSO}_3^- + \text{SO}_4^{2-} \rightarrow ([\text{ArNR}]^+ + \text{SO}_4^{2-})\text{ion pair} + \text{SO}_4^{2-} + \text{H}^+ \quad (7)
\]

This modified classic Behrmann’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 \( \text{S}_2\text{O}_8^{2-} \) nucleophilic displacement by the arylamine nitrogen on peroxide oxygen of \( \text{S}_2\text{O}_8^{2-} \), we here provide some additional arguments. In both proposed electron transfer and \( \text{S}_2\text{O}_8^{2-} \) nucleophilic displacement processes the initial reaction between arylamine and \( \text{S}_2\text{O}_8^{2-} \) is governed by the HOMO—LUMO interaction. The \( \text{S}_2\text{O}_8^{2-} \) nucleophilic displacement by the aniline nitrogen on peroxide oxygen of \( \text{S}_2\text{O}_8^{2-} \) 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 \( \pi^- \)-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 \( \text{S}_2\text{O}_8^{2-} \) nucleophilic displacement but electron transfer.

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**Figure 1.** Aniline HOMO computed by AM1/COSMO.

**Figure 2.** Peroxydisulfate dianion LUMO computed by AM1/COSMO.
It should also be noted that the $S\mathbf{2}$ nucleophilic displacement by any nucleophile on peroxide oxygen of $S\mathbf{2}O_8^{2-}$ is disputable since the peroxide $O\mathbf{-}O$ bond in $S\mathbf{2}O_8^{2-}$ 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 $S\mathbf{2}O_8^{2-}$ 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 $S\mathbf{2}O_8^{2-}$. 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 $S\mathbf{2}O_8^{2-}$.

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