Photooxidation of Methylbenzenes and Methylnaphthalenes Sensitized by Cyanoanthracenes

Angelo Albini* and Silvia Spreti
Dipartimento di Chimica Organica dell’Università, V. le Taramelli 10, 27100 Pavia, Italy
Z. Naturforsch. 41b, 1286–1292 (1986); received April 7, 1986
Photooxidation, Methylbenzenes, Methylnaphthalenes, Cyanoanthracenes

9-Cyanoanthracene, 9,10-dicyanoanthracene and 3,7,9,10-tetracyanoanthracene photosensitize the oxidation in acetonitrile of toluene, durene, hexamethylnaphthalene, 1-methyl- and 2-methyl-naphthalene to the corresponding aldehydes, with low yield of the alcohols and, in the case of hexamethylnaphthalene, of tetramethylphthalide. In benzene, only hexamethylnaphthalene reacts through a different pathway involving singlet oxygen. Comparison with fluorescence quenching data and experiments in the presence of good donors, halides or radical traps, as well as the effect of solvents and of oxygen concentration show that the reaction involves electron transfer from the methyralomeric to the singlet excited state of the sensitizer, followed by proton transfer to CA’ or O2•− yielding benzyl radicals, which react with oxygen or can be trapped.

1. Introduction

Reaction with singlet oxygen to yield 1,4-endoperoxides is a common occurrence among anthracenes as well as polymethylnaphthalenes [1, 2a], but it has not been reported in the benzene series except for sterically overcrowded hexamethylnaphthalene [2b] and electron rich derivatives such as phenols and phenylethers [3]. Photooxidation of alkyl aromatics at the benzylic position occurs by different mechanisms. These include radical processes initiated by hydrogen abstraction by triplet sensitizers (Type I photosensitized oxidation, eq. (1) [4, 5])

\[
\text{Sens}^* + \text{ArCH}_3 \rightarrow \text{Sens}^- + \text{ArCH}_2 \quad \text{(1)}
\]

as well as by direct irradiation of the change transfer complex between aromatic molecules and oxygen [5–8].

Recently, evidence has been put forward in favour of electron transfer photosensitized oxygenation of alkylaromatics. In particular, it has been reported that under sensitization by 9,10-dicyanoanthracene mono and dimethylnaphthalenes yield endoperoxides in apolar solvents (via singlet oxygen), and aldehydes and carboxylic acids in acetonitrile (via superoxide anion, eq. (2)) [9, 10]. However, no indication of the efficiency and the detailed mechanism of the two processes has been given. In a previous work photooxygenation of polymethylbenzenes with the same sensitizer in acetonitrile has been explained in terms of electron transfer, but the intervention of superoxide anion has been excluded [11].

\[
\text{Sens}^* + \text{ArCH}_3 \rightarrow \text{Sens}^* + \text{ArCH}_2 \rightarrow \text{Sens}^- + \text{O}_2 \quad \text{(2)}
\]

The aim of the present work is to investigate the scope of the electron transfer photosensitized oxygenation of methyralomaratics and to obtain a detailed mechanistic picture of this reaction on the basis of quantitative data.

2. Results and Discussion

In order to obtain results of general significance, three anthracene sensitizers were considered, viz. 9-cyano- (MCA), 9,10-dicyano- (DCA) and 3,7,9,10-tetracyanoanthracene (TCA). These molecules are similar in singlet excited state energy and lifetime [12, 13] as well as in their high fluorescence and low intersystem crossing quantum yield [14, 16] but largely differ in electron affinity [14, 17]. The substrates chosen were toluene (1), durene (1,2,4,5-tetramethylbenzene (2)), hexamethylnaphthalene (3), 1-(4) and 2-methylnaphthalene (5), i.e. two benzenes and two naphthalenes reputed of minimal reactivity with singlet oxygen in comparison with a reactive substrate, viz. hexamethylnaphthalene. In the first series of measurements, quenching of cyanoanthracenes (CA) fluorescence by substrates 1–5 in degassed acetonitrile and benzene was determined. No significant exciplex emission was observed. Linear plots for \(I/I_0\) vs substrate concentration were obtained in every case, and measured Stern Volmer constants

* Reprint requests to Prof. Dr. Angelo Albini.
Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0340–5087/86/1000–1286/5 0.01.00

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.
Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungstypen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.
On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.
Table I. Stern Volmer constants ($K_{sv}$, M$^{-1}$) for quenching of CA fluorescence.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>MCA</th>
<th>DCA</th>
<th>TCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E(A^+A), \text{V}$</td>
<td>-1.58$^a$</td>
<td>-0.98$^a$</td>
<td>-0.45$^b$</td>
</tr>
<tr>
<td>$E_{onset}, \text{eV}$</td>
<td>3.12$^c$</td>
<td>2.99$^c$</td>
<td>2.98$^c$</td>
</tr>
<tr>
<td>$\tau, \text{ns}$</td>
<td>17.2$^d$</td>
<td>15.3$^d$</td>
<td>19.6$^e$</td>
</tr>
</tbody>
</table>

Table II. Quantum yield of the photooxygenation of substrates 1-5.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent</th>
<th>Sensitizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene (1)</td>
<td>MeCN</td>
<td>MCA</td>
</tr>
<tr>
<td>Durene (2)</td>
<td>MeCN</td>
<td>MCA</td>
</tr>
<tr>
<td>Hexamethylbenzene (3)</td>
<td>MeCN</td>
<td>DCA</td>
</tr>
<tr>
<td>1-Methylnaphthalene (4)</td>
<td>MeCN</td>
<td>TCA</td>
</tr>
<tr>
<td>2-Methylnaphthalene (5)</td>
<td>MeCN</td>
<td>MCA</td>
</tr>
</tbody>
</table>

$^a$ In oxygen equilibrated solution. Values measured in air equilibrated solution differ by less than 10%. Product is the corresponding aldehyde with 0—5% of the alcohol. When no value is given, $\Phi < 1 \times 10^{-4}$; $^b$ products: 6, 45; 7, 3; 8, 25%; $^c$ products: 6, 84; 7, 2; 8, 12%; $^d$ only product 10.

Ksv are reported in Table I. In conjunction with literature available singlet state lifetimes and redox potentials (see Table I) rate constants for quenching ($k_q$) and free energy change for electron transfer from the substrates to singlet excited sensitizers ($\Delta G = E(D/D^0) - E(A^+A) - e^2/4\pi\epsilon a - E_{onset}$) [18] can be calculated. As expected, quenching constants level to a value of 1.3—1.7 $\times 10^{10}$ M$^{-1}$s$^{-1}$ for $\Delta G$ values largely negative (as it is the case for DCA with donors 2—5 and TCA with 1—5), while quenching is slower for $\Delta G$ slightly negative (MCA with donors 3—5) and negligible for $\Delta G$ positive.

Photooxygenation experiments were carried out at 400 nm (light absorbed only by the sensitizers, $10^{-4}$ M) on acetonitrile and benzene solutions of compounds 1—5 ($10^{-2}$ M). Conversion was limited to ca. 20% and product distribution was determined by g.l.c. and/or h.p.l.c.

Separated larger scale experiments gave similar results and allowed isolation of the products by column chromatography and their characterization. The results (Table II) can be summarized as follows. Sensitized irradiation in oxygen or air equilibrated acetonitrile leads in every case to the corresponding aldehyde, accompanied by minor amounts (1—5%) of the benzyl alcohol. Under this condition little, if any, of the benzoic acids is formed, whereas at high-

![Chemical structure](image)

MCA $X, Y = H$; DCA $X = \text{CN}, Y = H$; TCA $X, Y = \text{CN}$.
reverts to the components at r.t. Nor do we find products hypothetically arising from further reaction of an endoperoxide, such as 2-methylnaphthoquinone (9) from 5. A change in the reaction course is indeed observed in the case of hexamethylbenzene. Quantum yield is lower by an order of magnitude and the product is 8-endo-hydroperoxy-7-methylene-1,4,5,6,8-pentamethyl-2,3-dioxabicyclo[2.2.2]oct-5-ene (10), from 1,4 singlet oxygen addition followed by ene reaction, in accordance with the results of dye-sensitized photooxygenation [2b]. This reaction is not observed with TCA as sensitizer.

The role of CAs in the oxidation of methylaromatics is thus clearly defined. We [20], as well as others [12, 21–23], have shown that cyanoanthracenes yield singlet oxygen. Sensitization occurs via both singlet and triplet states (eqs (4, 5)). Spontaneous intersystem crossing is inefficient, and the limiting quantum yield (total quenching of the singlet by oxygen) is 2.

\[
\begin{align*}
CA^{1*} + O_2 & \rightarrow CA^{3*} + O_2^+ \quad (4) \\
CA^{3*} + O_2 & \rightarrow CA + O_2^+ \quad (5)
\end{align*}
\]

The oxygenation of alkenes sensitized by CAs does involve singlet oxygen, and the yield is proportional to the fraction of CA\(^{1*}\) quenched by oxygen [20].

The oxidation of methylaromatics is clearly different. Thus, except than with 3, reaction is observed only in polar solvents and with substrates significantly quenching the sensitizer singlet. The yield in oxygen equilibrated vs air equilibrated solution does not grow, as quenching by \(O_2\) does (e.g. from 1.8 to 9% in the TCA sensitized oxidation of 2) but changes little, as quenching by the substrate does (in the same example, from 65 to 61%). In fact, measurements in air equilibrated solutions are nearly indistinguishable from those in oxygen saturated solutions, in contrast with the oxidation of alkenes [20]. In principle, it is possible that the process is initiated by substrate quenching of CA\(^{1*}\), but this serves only to promote intersystemcrossing to CA triplet via radical ions recombination (eqs (6, 5)) or that the intermediate cispexplex sensitizes oxygen (eq. (7)).

\[
\begin{align*}
CA^{1*} + ArCH_3 & \rightarrow (CA^+ + ArCH_3^-) \rightarrow CA^{3*} + ArCH_3 \\
(CA\cdots ArCH_3)^* + O_2 & \rightarrow CA + ArCH_3 + O_2 \quad (6)
\end{align*}
\]

The latter possibility has been explicitly considered in the related case of the DCA photosensitized oxygenation of 1,4-dimethylnaphthalene [24–26]. However, it is unlikely that any such possibility applies in the present case, on account both of the occurrence of the reaction only in polar solvents and of the clear cut difference in the products obtained in the case of hexamethylbenzene, the only substrate which is oxidized both in acetonitrile (products 6–8) and benzene (product 10).

The electron transfer nature of the methyl aromatics oxidation is further supported by the quenching of

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sensitizer</th>
<th>Solvent</th>
<th>Products (quantum yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>DCA(^a)</td>
<td>CCl(_4)</td>
<td>None ((\Phi \ll 10^{-4}))</td>
</tr>
<tr>
<td>3</td>
<td>Benzanthrone(^b)</td>
<td>MeCN</td>
<td>10 ((\Phi = 0.011))</td>
</tr>
<tr>
<td>3</td>
<td>Benzanthrone(^b)</td>
<td>Benzene</td>
<td>10 ((\Phi = 0.009))</td>
</tr>
<tr>
<td>5</td>
<td>Direct irradiation(^b)</td>
<td>CHCl(_3)</td>
<td>2-Naphthaldehyde ((\Phi = 0.028))</td>
</tr>
</tbody>
</table>

Table III. Photooxidation in various conditions.

\(^a\) Irradiation at 400 nm;
\(^b\) irradiation at 313 nm.
Table IV. Effect of additives on the DCA photosensitized oxidation of durene (2) and 2-methylnaphthalene (5) in acetonitrile.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Substrate</th>
<th>2, 0.01 M</th>
<th>5, 0.01 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CCl₄, 0.003 M</td>
<td>2.5</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>CCl₄, 0.03 M</td>
<td>2.4</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>CCl₄, 0.15 M</td>
<td>2.6</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>1,4-Dimethoxybenzene, 1×10⁻⁴ M</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>2,6-Di-t-butylphenol, 5×10⁻⁴ M</td>
<td>0.01</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>p-Benzoquinone, 5×10⁻⁴ M</td>
<td>0.05</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

the reaction by good donors such as 1,4-dimethoxybenzene or amines at concentration low enough not to quench appreciably CA¹⁺, but certainly sufficient to reduce ArCH₃⁺ (Table IV).

It is also apparent that the reaction involves the intermediacy of benzyl radicals. This results from the similarity of the reaction course with that observed in methylbenzenes autoxidation [28] and irradiation of charge transfer complexes with oxygen [6] as well as from the quenching by radical scavengers, such as 2,6-di-t-butylphenol (Table IV) and the actual trapping of benzyl radicals by quinones. Thus, photosensitization of durene in degassed acetonitrile in the presence of p-benzoquinone yields 2,4,5-trimethylbenzyl-p-benzoquinone (11, 15%) as the only isolable product. Similar reaction of thermally created benzyl radicals are known [29].

On the basis of these data the reaction can be assumed to follow the scheme:

\[ \text{Sens}^{-} \rightarrow \text{CA}^{+} \rightarrow \text{ArCH}_{3}^{-} \rightarrow \text{ArCH}_{3}^{-} \rightarrow \text{Products} \]

where \( p_1 \) and \( p_2 \) are the probabilities that the initial exciplex yields a solvent stabilized pair of radical ions and that the latter yields the benzyl radical. Neither quantity is influenced by oxygen dissolved (above ca. 2×10⁻³ M) or by substrate concentration. Thus, the chemical quantum yield is

\[ \Phi = \frac{p_1 p_2 k_{s} [\text{ArCH}_{3}]}{k_{d} + k_{s} [\text{ArCH}_{3}]} \]  

(8)

or in the inverse form:

\[ \Phi^{-1} = \frac{1}{p_1 p_2} \left( 1 + \frac{k_{d}}{k_{s} [\text{ArCH}_{3}]} \right) \]  

(9)

A double reciprocal plot of reaction quantum yield vs donor concentration yields a straight line, the intercept being a measure of \( 1/p_1 p_2 \). The ratio intercept/slope is the same quantity \( k_{q}/k_{d} \) obtained from fluorescence quenching (\( K_{sv} \)). Fig. 1 shows the verification of eq. (9) for the DCA sensitized photooxidation of 2. The limiting quantum yield is \( \Phi_{\text{lim}} = p_1 p_2 \approx 0.52 \), and for the ratio \( k_{q}/k_{d} \) the value 95 M⁻¹ is obtained, in reasonable agreement with the value from fluorescence quenching (115 M⁻¹ in oxygen equilibrated solution). The probability \( p_1 \) is significant only in polar medium and strongly depends on the structure of the donor. Better orbitals overlap makes the donor-acceptor contribution less important for methylnaphthalenes-CA exciplexes, so that \( p_1 \) is much lower than in the benzene series, and so is photo-oxygenation. Conversely, the same factor makes photocycloaddition (in oxygen free solution) possible in the first but not in the latter case.

Understanding of the following step, leading to benzyl radicals, and of the factors influencing \( p_2 \) in less straightforward. A possible mechanism is quenching of radical anion \( \text{CA}^{+} \) by oxygen and following proton transfer

\[ \text{CA}^{+} + \text{O}_2 \rightarrow \text{CA} + \text{O}_2^{+} \]  

(10)

\[ \text{O}_2^{+} + \text{ArCH}_{3}^{-} \rightarrow \text{OOH}^{-} + \text{ArCH}_2 \]  

(11)

A support for this view comes from the lower (by a
factor of 3 to 10) efficiency of TCA as sensitizer as compared to DCA. This can be rationalized on the basis of the positive $\Delta G$ for the electron transfer in eq. (10) in the first case [17] as opposed to the largely negative $\Delta G$ in the latter one.

Unambiguous identification of the role of superoxide anion in the present reaction is difficult; $p$-benzoquinone, a known trap of superoxide [30–31], does quench the photooxidation, but, as mentioned above, this could as well be due to the chemical quenching of benzyl radicals. On the other hand, Saito et al. did not observe under these conditions [11] the cleavage of phenyl esters that would be expected in the presence of $O_2^-$ [32]. It is thus more appropriate to think that oxygen quenches the charge transfer excited complex, rather than "free" solvated radical anions, yielding a new radical ions pair, the same that is formed by excitation of the ground state charge transfer complex between the aromatic molecule and oxygen.

\[(CA^-⋅ArCH_3^-)^n + O_2 \rightarrow CA^+ + (ArCH_3^-⋅O_2^-)\]  

Subsequent proton transfer according to eq. (11) is, as pointed out by Onodera et al. [8], a facile process, and thus it is likely that no appreciable concentration of quenchable superoxide anion builds up. An alternative mechanism is proton transfer within the original radical ions pair, directly yielding benzyl radicals.

\[(CA^-⋅ArCH_3^-) → CAH^- + ArCH_2^+\]  

At least a part of the process follows this pathway as benzyl radicals are formed, and trapped, even in the absence of oxygen in the DCA sensitized reaction of durene (see above), unless the quinone behaves exactly like oxygen (eqs (12, 11)) and quenches the exciplex. More generally, CAs are consumed when irradiated with methyl aromatics in degassed solution, while they are completely recovered after extensive methyl aromatics photooxygenation.

The photooxidation is accelerated in the presence of halogenated compounds. The effect is apparent at low concentration of the additive, and is appropriately referred to quenching of the exciplex competing with fast back electron transfer, rather than to a radical chain mechanism, as suggested in ref. [11], as the latter would require the formation of benzyl chloride along with benzaldehyde.

\[(CA^-⋅ArCH_3^-) + CCl_4 \rightarrow CA + (CCl_3^- + ArCH_3^-) \rightarrow ArCH_2^+\] 

And higher concentration of carbon tetrachloride (or chloroform) the efficiency of the process decreases, as the additive interferes with the further radical course of the reaction, and no sensitized photooxidation is observed in neat CCl_4 (Tables III, IV). The effect of halogenated solvent becomes determining in the unsensitized reaction. Thus, photooxygenation of 1-methylnaphthalene by direct irradiation, a reaction first reported in 1972 by Rigandy [33], involves excitation of the ground state complex of 4 with oxygen and is much more efficient in halogenated than in other, either polar or apolar, solvents, as eq. (15) is the only alternative to physical decay for the excited complex.

\[(ArCH_3^-⋅O_2^-) \xrightleftharpoons[\text{hr.}]{\text{CCl}_3^+} \text{ArCH}_3^+ + \text{CCl}_3^- + O_2 \rightarrow \text{ArCH}_2^+\]  

3. Conclusion

From the present and previous work it is concluded that cyanoanthracenes sensitized photooxidation occurs according to either of the following pathways: i. Direct oxygen sensitization when the substrate is a (relatively) poor quencher of the CAs singlet excited state (eqs (4, 5)) and a good singlet oxygen acceptor; this is the case with simple alkenes [20, 22] and hexamethylbenzene in apolar medium, ii. Electron abstraction from the substrate, when this has opposite characteristics. In the case of methylbenzenes and monomethylnaphthalenes electron transfer is followed by proton transfer to either CA$^-$ or O$_2^-$, yielding a benzyl radical, which is the active species in the oxidation. iii. Indirect oxygen sensitization when the substrate is both a good quencher and a good singlet oxygen acceptor. This is the case for dimethyl- [10, 24] and, predictably, polymethylnaphthalenes. Singlet oxygen is indirectly formed by sensitization either from the exciplex (eq. (7)) or from CA triplet arising from ions recombination (eqs (6, 5)).

Experimental

Materials

MCA, substrates 1–5 1,4-dimethoxybenzene, 2,6-di-$t$-butylphenol, and $p$-benzoquinone were commercial products. DCA and TCA were prepared and purified according to literature procedures [13]. Spectroscopic grade solvents were used as received.
Fluorescence measurements

Fluorescence intensities were measured by means of an Aminco Bowman MPF spectrophotofluorimeter. Solutions were degassed by five freeze-degas-thaw cycles at $<10^{-4}$ torr. Fluorescence quenching in the presence of substrates 1–5 gave in every case linear Stern Volmer plots.

Quantum yield measurements

Solutions were prepared in 1 cm i.d. serum capped tubes, and, when appropriate, flushed for 15 min with purified nitrogen or oxygen. Irradiation was accomplished at 22 °C in a merry go round inserted in an Applied Photophysics multilamp apparatus fitted with twelve fluorescent lamps mod. 3026 (peak intensity at 410 nm, range 370–450 nm). Substrate consumption and products formation were determined by g.l.c. (Hewlett-Packard instrument, Carbowax 20% or SP 2100 3% columns) and/or h.p.l.c. (Waters instruments µ-Bondapack columns) in comparison with authentic samples. Light flux was measured by ferrioxalate actinometry. A series of experiments with different irradiation times were carried out, the maximum conversion achieved being less than 20%. Within these limits conversion and products formation are linear with time. Quantum yield does not depend on light intensity (flux $0.5–2 \times 10^{-6}$ Einstein cm$^{-2}$min$^{-1}$). Separate experiments in spectrophotocouvettes illuminated by means of a high pressure mercury arc were carried out and monochromatized at 400 nm by means of an interference filter gave not appreciably different results.

Preparative irradiation

These were carried out in an immersion well apparatus by means of a Pyrex filtered medium pressure mercury arc. The solution was evaporated and chromatographed on silica gel eluting with appropriate cyclohexane, benzene, ethyl acetate mixtures. Products were recognized by comparison with authentic samples. Pentamethyl benzaldehyde was prepared according to literature [34] and pentamethylbenzyl alcohol by sodium borohydride reduction of the former. Product 10, however, was directly determined by NMR on the reaction mixture as corresponding to literature data [2b].

2-(2,4,5-Trimethylbenzyl)-p-benzoquinone (11)

A solution of 3.5 mg DCA, 100 mg durene, and p-benzoquinone in 80 ml acetonitrile was degassed by boiling and cooling under Argon and irradiated by means of a Pyrex filtered medium pressure arc for 6 h. The irradiation mixture was evaporated and chromatographed on silica gel eluting with benzene cyclohexane mixtures to yield 3.5 mg DCA, 10 mg unreacted durene and 24 mg (15% yield) of the title compound, colourless needles from cyclohexane, m.p. 178 °C.

Analysis for $C_{10}H_{10}O_2$

Calcd  C 79.97  H 6.71.
Found  C 79.5  H 6.48.

NMR (CDCl$_3$): $\delta$ 2.15 s (1 Me), 2.25 s (2 Me), 3.7 d (CH$_2$), 6.15 q (H$_3$), 6.8–7 (3 H). $\nu$ IR (KBr): 1655 cm$^{-1}$.

This work was carried out in the frame of the special project on fine chemistry by CNR, Rome. One of us (S. S.) thanks ENI, Rome, for a fellowship.
[26] This is not the case with alkenes. With those compounds substrate quenching of CA\(^{1+}\) does not lead to CA\(^{2+}\), ref. [20].