REACTIONS OF ALKYL PEROXYL RADICALS WITH ZERO-VALENT IRON AND COBALT POWDERS IMMERSED IN AQUEOUS SOLUTIONS

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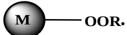
Methyl-peroxyl radicals formed radiolytically, react in fast reactions with the surfaces of Fe(0) and Co(0) powders immersed in aqueous solutions. The results suggest that the product of these reactions is . These transients decompose differently for different metals, *i.e.* for M = Fe the main product is CH_2O whereas for M = Co it is probably CH_3OH. The results point out that alkyl-peroxyl radicals formed in the course of degradation of organic compound near the surface of Zero-Valent Iron (ZVI) in aerated solutions react with the metal surface. These reactions have to be considered in the analysis of the mechanism of degradation of organic pollutants by Fe^0.

Keywords: Zero-Valent Iron, Permeable Reactive Barriers, Radicals, Peroxyl, Aqueous Solutions, Radiolysis.

Introduction

In the last years, the development of innovative methods for remediation of ground water contaminated by organic pollutants and bacteria are of significant priority. Zero-valent iron has been found to be highly effective in enhancing the rate of degradation of a wide range of organic contaminants compounds [1 – 4], including halo-organic compounds in aqueous solution [5 – 8].

The commonly implemented technology uses permeable reactive barriers (PRBs) filled with reactive materials, zero-valent iron is the most common reactive material used to intercept and decontaminate plumes in the subsurface or in batch processes [9 – 14]. Two basic mechanisms are involved in the interaction of zero valent iron, ZVI, with pollutants:

1. *Oxidation of the pollutant in aerated media*

Two slightly different mechanisms are commonly proposed for these oxidations [1 – 4, 15],

a.

$$Fe^0 + O_2 \rightarrow Fe^{2+} + O_2^{2-} \qquad (1)$$

$$O_2^{2-} + 2H^+ \rightarrow H_2O_2 \qquad (2)$$

$$Fe^0 + H_2O_2 \xrightarrow{2H^+} Fe^{2+} + 2H_2O \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \qquad (3)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{IV}{=}O^{2+} + H_2O \qquad (4)$$

$$OH^{\cdot}/Fe^{IV}{=}O^{2+} + RH \rightarrow H_2O/Fe^{III}OH^+ + R^{\cdot} \qquad (5)$$

Naturally when RH is an unsaturated compound $OH^{\cdot}$ adds to the unsaturated bond forming another organic radical.

b. Adding the following reactions

c.

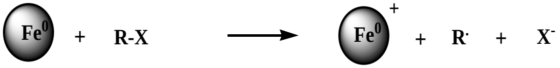
$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\cdot -} \qquad (6)$$

$$Fe^{2+} + O_2^{\cdot -} \xrightarrow{2H^+} Fe^{3+} + H_2O_2 \qquad (7)$$

as an additional mechanism of oxidation of the Fe^{2+} formed via reaction (1).

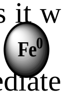
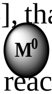
2. *Reduction of the pollutant, e.g. halo-organic pollutants*

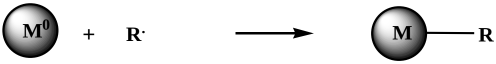
In this case it is commonly accepted that the first reaction occurring is [16, 17].



(8)

In both mechanisms organic radicals, $R^{\cdot}$, of one type or another are key intermediates in these processes. Commonly it is assumed that the final products stem from the follow up reactions of these radicals in the "homogenous" solutions.

However, in few reports it was shown [16, 18], that alkyl radicals $R^{\cdot}$, formed near the surface of  or other metals, , react with the metal particles to form intermediates, via the general reaction



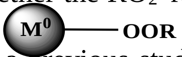
(9)

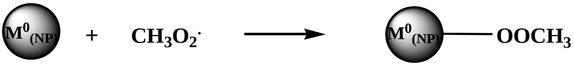
The final products in this case depend on the nature of M and of $R^{\cdot}$ and on the composition of the solution, the temperature *etc*. Thus reaction (9) has to be considered in all the systems where ZVI is used to remediate polluted aqueous solutions.

Furthermore, it should be noted that in aerated solutions the organic radicals $R^{\cdot}$, formed in reactions (5) and (8) react with dioxygen via

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \qquad (10)$$

The rate constant k_{10}, for most alkyl radicals approaches the diffusion controlled limit [19], *i.e.* $k_{10} \geq 10^9\ M^{-1}s^{-1}$ to form peroxyl radicals.

Therefore, it seemed of interest to study whether the $RO_2^{\cdot}$ radicals also react with  to form transients of the type  . This possibility seemed reasonable as it was shown in a previous study [20] that Ag^0 and Au^0 nano-particles react with $CH_3O_2^{\cdot}$ radicals via,



(11)

and that the rate constant of reactions (11) approaches the diffusion controlled limit[20]. It was therefore decided to study the reactions of $CH_3O_2^{\cdot}$ with Fe(0) and Co(0) powders.

Results and Discussion

Reaction between the Metal powders and the methyl peroxyl radicals

Small glass bulbs (15 mL) containing 10 g of metal (iron or cobalt) powders immersed in 2.5 mL of an aqueous solution containing 0.050 M $(CH_3)_2S{=}O$, sealed with a rubber septum and saturated by $N_2O{:}O_2$ (70:30 v/v) were irradiated in a γ source by a total dose of 480 Gy (48 krad). The blank solution was identical but without metals, *i.e.*, an aqueous solution of 0.050 M $(CH_3)_2S{=}O$, pH 4.0. After the irradiation the yield of formaldehyde was determined. The results are summed up in Table.

Table

Reactions between the methyl peroxyl radicals and metal powders [a], radiation-dose: 480 Gy (48,000 rad)

Sample	Irradiation	CH_2O (M)	G Value (±10%)	Yield (% of $\cdot OH/CH_3OO^{\cdot}$)
0.050 M $(CH_3)_2S{=}O$ (blank)	+	1.32×10^{-4}	2.75	46 %
Fe^0 powder + $(CH_3)_2S{=}O$[a]	+	1.72×10^{-4}	3.58	60%
Co^0 powder + $(CH_3)_2S{=}O$[a]	+	6.6×10^{-5}	1.36	23%
$FeSO_4$ + $(CH_3)_2S{=}O$[b]	+	1.33×10^{-4}	2.78	45%
Fe^0 powder + $(CH_3)_2S{=}O$[c]	--	$\le0.1\times10^{-4}$	-	-

[a] 10.0 gr metal powder, 2.5 ml $(CH_3)_2S{=}O$ 0.050 M pH 4.0, N_2O/O_2 saturated. G value is the number of molecules/species of a radiolytic product per 100 eV absorbed in the medium. The G values given herein are for the energy absorbed in the aqueous solution only.

[b] 2.5 mL of N_2O/O_2 saturated solutions containing $FeSO_4$ (5.0×10^{-4} M), $(CH_3)_2SO$ (0.05 M), pH 4.0.

[c] No irradiation, same treatment (including duration) and composition as [a]; this experiment proves that CH_2O is formed by the radiolytic process.

It is known that in the absence of a substrate, the methyl-peroxyl radicals decompose via a bimolecular reaction in which a short lived dimmer transient is formed [21]:

$$2CH_3OO^{\cdot} \rightarrow CH_3OOOOCH_3 \rightarrow \text{products} \quad 2k_{12}\ [22] = 8\cdot10^{8}\ M^{-1}s^{-1} \qquad (12)$$

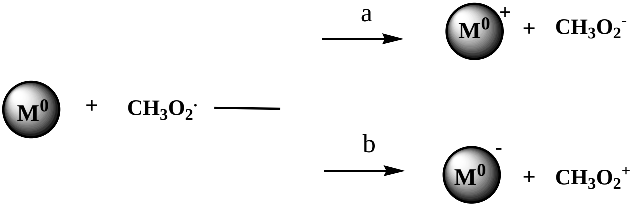
This dimmer decomposes into a variety of final products where the major product is CH_2O with a yield of ca. 50% at pH 4.0 [21, 23], *i.e.* $G(CH_2O) \sim 3.0$. Indeed, in the blank experiments, Table 1 (sample 1), CH_2O is formed with a yield of $G = 2.8$.

The addition of iron and or cobalt powders changes the CH_2O yield considerably. However, the two metals affect the CH_2O yield differently;

the cobalt powder decreases the yield whereas the iron powder increases it. These results clearly demonstrate that the $CH_3O_2\cdot$ radicals react with the metal powders. Other blank experiments, Table 1, prove that no, or very little, CH_2O is formed thermally in these experiments and that the CH_2O is not formed via a reaction of the $CH_3O_2\cdot$ radicals with $Fe(H_2O)_6^{2+}$.

The next question is what are the mechanisms of reaction of the $CH_3O_2\cdot$ radicals with the metal powders? In principle two mechanisms are possible:

a. An "outer sphere" mechanism:



(13)

Reaction (13a) will be followed by:

$$CH_3O_2^- \xrightarrow{H^+} CH_3OOH \rightarrow CH_2O + H_2O \qquad (14)$$

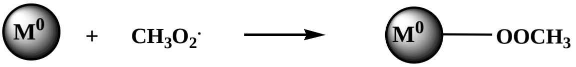
i.e. the CH_2O yield will increase, whereas reaction (13b), (which is not reasonable as the $CH_3O_2\cdot$ radicals are strong oxidizing agents and are therefore not expected to reduce the metal particles), would be followed by:

$$CH_3O_2^+ \xrightarrow{-O_2} CH_3^+ \xrightarrow{H_2O} CH_3OH + H^+ \qquad (15)$$

and decrease the CH_2O yield.

Thus, the mechanism outlined in reaction (13a) could fit the iron system but not the cobalt one. The results for the cobalt system are in accord with reaction (13b) which however is not reasonable as explained above. Therefore, at least for Co^0, as for Ag^0 and Au^0 [20], and thus probably also for Fe^0 the "inner sphere" mechanism has to be considered.

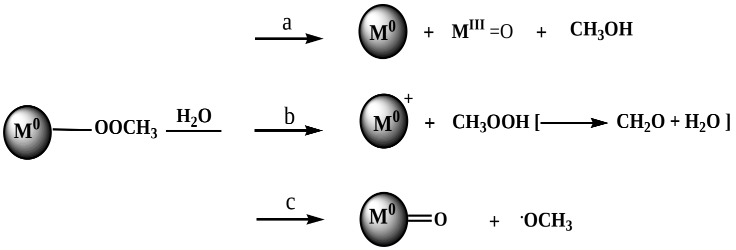
b. An "inner sphere" mechanism:



(16)

That is, the formation of a transient with a metal-oxygen σ bond in analogy with the mechanism reported for the reactions of alkyl radicals with metal surfaces [18].

Reaction (16) will be followed by:



(17)

Reaction (17c), which corresponds to the homolytic O-O bond scission, will be followed by either

$$CH_3O\cdot + (CH_3)_2SO \rightarrow CH_3OH + CH_2(CH_3)SO\cdot \qquad (18)$$

or more probably by [24a]

$$CH_3O\cdot \rightarrow CH_2OH\cdot \qquad k \sim 5\cdot 10^6\ s^{-1}\ [24b] \qquad (19)$$

followed by:

$$CH_2OH\cdot \xrightarrow{O_2} O_2CH_2OH\cdot \rightarrow CH_2O + HO_2\cdot \qquad (20)$$

Thus, the results for the cobalt system fit a mechanism involving reaction (16) followed by reaction (17a) or by reaction (17c) provided that reaction (18) is faster than reaction (19) under the experimental conditions.

For the iron system it is proposed that the mechanism involves reaction (16) followed by reaction (17b) or by reaction (17c) followed then by reactions (19) and (20).

Analysis of the total Fe ions dissolved in the solution before and after the reaction was performed using ICP, as expected the concentration increased after irradiation. The measured value was found to be $3.5\cdot10^{-4}$ M. The calculated stoichiometric concentration of Fe^{2+} due to reactions (16) followed by reaction (17), which yields $1.72\cdot10^{-4}$ M CH_2O in the irradiated system is expected to be is $8.6\cdot10^{-5}$ M.

The latter is less than the one measured and this is apparently due to the contribution of the corrosion of iron in water in the presence of oxygen:

$$2Fe^{\circ}_{(s)} + O_{2\,(aq)} + 2H_2O \leftrightarrows 2Fe^{2+}_{(aq)} + 4OH^- \qquad (21)$$

Next it was checked whether the CH_2O is formed via reactions:

$$Fe^{2+}_{(aq)} + OOCH_3\cdot \rightarrow (H_2O)_5Fe^{III}\text{-}(O_2CH_3)^{2+} \qquad (22)$$
$$(H_2O)_5Fe^{III}\text{-}(O_2CH_3)^{2+} + H_3O^+ \rightarrow Fe^{3+}_{(aq)} + CH_2O + H_2O \qquad (23)$$

For this purpose, N_2O/O_2 saturated solutions containing $FeSO_4$ ($5\cdot10^{-4}$ M) and $(CH_3)_2SO$ (0.05 M) were irradiated. The results (see sample 4, Table 1) clearly indicate that reactions involving the $Fe^{2+}_{(aq)}$ ions, formed in the corrosion process, are not the source of the formaldehyde formed in the presence of the iron powder. The latter conclusion is in accord with previous kinetic study of this reaction [24c].

Conclusions

The results obtained in this study demonstrate that $CH_3O_2\cdot$ radicals, and therefore probably also other alkyl-peroxyl radicals, react in fast reactions with the surface of zero-valent iron and cobalt. The intermediates thus formed on the surface, M^0-$OOCH_3$, decompose via heterolysis of the metal-peroxo bond, for M = Fe, to yield $CH_3OOH/(CH_2O + H_2O)$; on the other hand for M = Co the transient decomposes via heterolysis of the O-O bond. These results are only qualitative, and further experiments should be performed in order to elucidate the detailed reaction mechanisms.

These observations are relevant to elucidate the role of zero-valent iron and its use in the presence of O_2 for the degradation of organic contaminates in remedial applications.

Furthermore, the results reported herein and those recently reported for the reactions of noble nano-particles with $CH_3OO\cdot$ radicals, point out that the mechanisms of decomposition of the transients M^0-OOR, formed in those reactions depend on the nature of M and probably also on the nature of R·, the pH *etc.*

Experimental section

All the chemicals used this study were of A.R. grade and were used without further purification. The water used was deionized and further purified by a Millipore Milli-Q setup with a final resistivity of >10 MΩ/cm. The metal powders used in this study were Fe^0 powder Merck (99%, ≤ 10 μm) and Co powder Alfa Aesar (99.5, -325 mesh).

2.5 mL of the aqueous solution (0.050 M $(CH_3)_2S{=}O$, pH 4.0) were added to a glass bulb (15 ml) sealed with a rubber septum containing 10 g of the metal powder, thus the solutions were in between the metal particles.

The blank solution was identical but without a metal powder. Prior to the irradiation, the samples were saturated with a gas stream of N_2O/O_2 (70:30 v/v) for 15 minutes using two needles through the septum. The solutions were irradiated to the appropriate dose using a ^{60}Co γ source of Noratom Gamma cell, which emits γ-rays of 1.1 MeV at a dose rate of 20 Gy/min.

The resultant formaldehyde was measured spectrophotometrically after filtration of the powders, using the acetylacetone/ammonium acetate method [25] (Hantzsch reaction) in which the yellow colour at λ=412 nm is measured due to the formation of diacetyl-dihydro-lutidine. It should be noted that the duration of each experiment from the moment the metal powders was immersed in the solution till analysis was always < 3 hrs.

Radiation induced production of methyl peroxyl radicals: When ionizing radiation (γ –radiation, 20 Gy/min) is absorbed by dilute aqueous solutions the following initial products are formed [26]:

$$H_2O \xrightarrow{\gamma, e^-} H\cdot\ (0.60),\ OH\cdot\ (2.65),\ e^-_{aq}\ (2.65),\ H_2O_2\ (0.75),\ H_2\ (0.45) \quad (24)$$

Where the numbers given in parentheses are G values (G values are defined as the number of molecules of each product per 100 eV of radiation absorbed by the solution). In concentrated solutions the yields of OH· and e^-_{aq} are somewhat higher and those of H_2O_2, H_2 and H· are somewhat lower. In N_2O-saturated solutions the hydrated electron is converted into the hydroxyl radical via [27]:

$$e^-_{aq} + N_2O \rightarrow N_2 + OH\cdot + OH^- \qquad k_{25} = 8.7\cdot10^9\ M^{-1}s^{-1} \qquad (25)$$

Thus, at pH > 3 the hydrated electrons react with N_2O yielding $\cdot OH$ as the major radical.

The $\cdot OH$ radicals are converted into methyl radicals upon the reaction with dimethylsulfoxide via the following reactions [28]:

$$OH\cdot + (CH_3)_2S{=}O \rightarrow (CH_3)_2\overset{\bullet}{S}(O)OH \quad k_{26} = 7.0\cdot10^9\ M^{-1}s^{-1} \qquad (26)$$

$$(CH_3)_2\overset{\bullet}{S}(O)OH \rightarrow (CH_3)S(O)OH + CH_3\cdot \quad k_{27} = 1.5\cdot10^7\ s^{-1} \qquad (27)$$

In solutions containing N_2O, $(CH_3)_2S{=}O$ and dioxygen, the methyl radicals are converted into methyl peroxyl radicals [29] (28) while the H· atoms which are produced via reaction (24) react with dioxygen. The $HO_2\cdot$ radical, thus formed, is in equilibrium with its deprotonated form (pKa = 4.7) [30]:

$$CH_3\cdot + O_2 \rightarrow CH_3OO\cdot \quad k_{28} = 3.7\cdot10^9\ M^{-1}s^{-1} \qquad (28)$$

$$H\cdot + O_2 \rightarrow HO_2 \leftrightarrows H^+ + O_2\cdot^- \quad k_{29} = 2.1\cdot10^{10}\ M^{-1}s^{-1} \qquad (29)$$

It should be noted that due to the much higher solubility of N_2O ($2.4\cdot10^{-2}$ M) compared to that of O_2 ($1.3\cdot10^{-3}$ M) and the volume ratio of these gases under the experimental conditions ($N_2O:O_2$ = 70:30 v/v), the reaction of the hydrated electron with the dioxygen is negligible and almost complete conversion of $e^-_{(aq)}$ into OH· radicals is achieved and G (OH·) = 6.

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