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Photoproduction of hydroxyl radicals from Fe(III)-hydroxy complex: a quantitative assessment

Jiju M. Joseph, Rani Varghese, C.T. Aravindakumar*

School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686560, Kerala, India

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Abstract

Photolysis of aqueous solutions of ferric perchlorate in the presence of methanol, benzene and 2-deoxy-D-ribose at low pH has been investigated using sunlight and UV light in order to quantitatively assess the involvement of hydroxyl radicals ($^{\bullet}$OH) in the photolysis of Fe(III)-hydroxy complexes. Time-dependent formation of formaldehyde, phenol and thiobarbituric acid-reactive substance (TBA-RS) was observed in the presence of methanol, benzene and 2-deoxy-D-ribose, respectively. The observed quantum yields of formaldehyde, phenol and TBA-RS are 0.025, 0.0098 and 0.0038, respectively, using UV light. A slightly lower quantum yields are obtained with sunlight owing to its lower intensity. The mechanistic aspects of these reactions are proposed based on the formation of $^{\bullet}$OH from the photo-excited $Fe(OH)^{2+}$ complex and their subsequent reactions with methanol, benzene and 2-deoxy-D-ribose. The quantum yield of $^{\bullet}$OH is calculated from the observed quantum yields of formaldehyde, phenol and TBA-RS based on the reported percentage contribution of $^{\bullet}$OH in the formation of these products using radiation chemical techniques from the respective reactions. The calculated quantum yields of $^{\bullet}$OH were in the range 0.018–0.025 and 0.014–0.018 with UV light and sunlight, respectively. The results obtained with the photolytic studies have been compared with those from radiation chemical studies.

Keywords: $Fe(OH)^{2+}$; Hydroxyl radical; Electron transfer; Organic radical; Quantum yield; Photochemical; Radiation chemical

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1. Introduction

There is a growing concern in the development of new methodologies for the degradation of toxic water pollutants in recent years. Although the conventional methods such as adsorption on activated carbon, flocculation, filtration and biodegradation can remove such pollutants from water to certain extent, they are mostly inefficient to degrade stable aromatics. Advanced oxidation processes (AOPs) are generally accepted as potential solutions to this problem since these involve generation of a powerful oxidizing agent, the hydroxyl radicals ($^{\bullet}$OH) which can effectively degrade most of the organic pollutants [1]. The most commonly used AOPs include photo-decomposition of hydrogen peroxide (H_2O_2/UV) [2], photolysis of ozone (O_3/UV) [3], photo-catalysis (TiO_2/UV) [4], Fenton and photo-Fenton reactions (Fe^{2+}/H_2O_2/UV) [5–7], radiolytic technique [8] and sonochemical method [9].

It is known that photolysis of Fe(III)-hydroxy complexes can produce hydroxyl radicals at acidic pHs [10,11]. This system has been widely explored for the degradation of organic contaminants in aqueous medium [12,13]. The most predominant photo-active monomeric Fe(III)-hydroxy complex in the pH range 2.5–5.0 is the $Fe(OH)^{2+}$ [10]. An advantage of this system is that its CTC band strongly overlaps with the solar UV spectrum (290–400 nm) and therefore can be easily photolyzed using sunlight. Photolysis of these complexes can yield $^{\bullet}$OH which is believed to be formed as a result of electron transfer from the ligand (OH^-) to Fe(III) in the excited states (reaction (1)):

$$Fe(OH)^{2+} + h\nu \rightarrow [Fe(OH)^{2+}]^* \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (1)$$

It is reported that the major source of hydroxyl radicals in rain, cloud and fog is by the photolysis of Fe(III)-hydroxy complex under a similar mechanism [10]. Based on this principle, a considerable attempt has been made to investigate the degradation of organic pollutants such as chlorophenols and triazines [12,14,15]. Both sunlight and UV light were found to be effective for these reactions [12]. However, there could be an alternate mechanism for the degradation of pollutants without the involvement of hydroxyl radicals as reported by Zuo and Hoigne [16]. This is suggested as a result of a direct electron transfer from the organic ligand to Fe(III) in the excited Fe(III)-organo complexes, formed between Fe(III) and the organic compounds [16]. This results in the formation

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* Corresponding author. Fax: +91-481-597731.
E-mail address: mgu@md2.vsnl.net.in (C.T. Aravindakumar).

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of Fe(II) and an organic radical which on further oxidation in the presence of oxygen may lead to its degradation or transformation into other products [16] (reaction (2)):

$$\text{Fe(III)-org complex} + h\nu \rightarrow [\text{Fe(III)-org complex}]^* \rightarrow \text{Fe(III)} + \text{organic radical} \qquad (2)$$

Although the above two mechanisms would ultimately lead to the decomposition of organic molecules as widely reported [12,16], it is obvious that there exists quite some ambiguity in the exact reaction mechanism of the above process. Therefore, the main objective of this study is to reinvestigate the photolysis of Fe(III)-hydroxy complex in order to quantitatively assess the involvement of $^{\bullet}OH$ using some of their well-known typical reactions. Both sunlight and UV light were used for the photolysis. The selected typical reactions include: (i) formation of formaldehyde from methanol, (ii) formation of phenol from benzene, and (iii) formation of a thiobarbituric acid-reactive substance (TBA-RS) from 2-deoxy-D-ribose. The results obtained with these reactions were compared with those from radiation chemical methods which is considered as a clean source of hydroxyl radicals.

2. Experimental

Commercially available high-purity methanol, 2-deoxy-D-ribose, thiobarbituric acid, ferric sulfate, potassium oxalate, acetylacetone and potassium ferricyanide have been used without further purification. Ferric perchlorate was synthesized from ferric chloride and sodium carbonate in the presence of perchloric acid. All solutions were prepared using triply distilled water. The concentration of ferric perchlorate used in all the experiments was 10^{-2} mol dm^{-3}. For the estimation of formaldehyde, phenol and TBA-RS, the irradiated solutions typically contained 1 mol dm^{-3} methanol, 1×10^{-3} mol dm^{-3} benzene and 1×10^{-2} mol dm^{-3} 2-deoxy-D-ribose, respectively. The pH of the ferric perchlorate system was between 2.5 and 3 for all the experiments carried out in this work.

Photolysis was performed using both sunlight and UV light. Irradiations using sunlight were carried out in the middle of a bright sunny day (April/May at Kottayam, Kerala, latitude 9°5′N). A high pressure mercury vapour lamp was used for UV irradiation. The test tubes containing solutions were kept in dark before and after irradiation. Intensity of the UV lamp was determined using ferrioxalate actinometry [17]. Ferrioxalate solution was prepared before irradiation by mixing equal volumes of ferric sulfate (0.012 mol dm^{-3}) and potassium oxalate (0.036 mol dm^{-3}). The intensity of the UV lamp was found to be 9.4×10^{16} ein s^{-1} cm^{-3}. Quantum yields of the products were calculated in comparison with the actinometry values. In the case of reactions performed using sunlight, actinometry was performed simultaneously with the samples to avoid the error due to changes in intensity of light. Gamma radiolysis experiments were carried out using a ^{60}Co-γ source. The dose rate was determined using Fricke dosimetry [18].

Formaldehyde (HCHO) was estimated as its acetyl acetone derivative at 412 nm ($\varepsilon = 7530$ dm^{-3} mol^{-1} cm^{-1}) [19]. Thiobarbituric acid assay (TBA assay) was performed by mixing equal volumes of the irradiated samples which contained 2-deoxy-D-ribose (DR) with 1% TBA and 2.8% HCl [20]. The pink-colored chromogen (TBA-chr) has an absorption coefficient of 1.53×10^4 dm^3 mol^{-1} cm^{-1} at 532 nm. Fe(II) was determined by photometric method using 1,10-phenanthroline as the color-producing reagent which can form a red-colored complex that absorbs at 510 nm ($\varepsilon_{510\,\mathrm{nm}} = 1.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}) [17]. Spectroscopic analysis was done on a UV–Vis spectrophotometer (Shimadzu). The formation of phenol from benzene was monitored at 220 nm using HPLC (Shimadzu LC-10AS) with UV–Vis detector (Shimadzu SPD 10A). The eluent was 40% acetonitrile at a flow rate of 1 ml/min using Nucleosil, C-18 column.

3. Results and discussion

In order to quantitatively assess the formation of $^{\bullet}OH$ in the ferric hydroxy system, photolysis of aqueous ferric perchlorate (10^{-2} mol dm^{-3}) were carried out in the presence of methanol (1 mol dm^{-3}), benzene (10^{-3} mol dm^{-3}) and 2-deoxy-D-ribose (10^{-2} mol dm^{-3}) using sunlight and UV light. The mechanism of these reactions are well understood using radiation chemical techniques. Furthermore, the formation of the end product of these reactions, if $^{\bullet}OH$ is the major reactive species, can be easily determined using normal analytical techniques. The results obtained with these three systems are described below.

3.1. Formation of formaldehyde from methanol

Photolysis of ferric perchlorate was carried out in the presence of methanol using sunlight and UV light and the amount of formaldehyde formed was determined at different time intervals. A time-dependent increase in the yield of HCHO was observed and this time dependence using both sunlight and UV light is shown in Fig. 1. It was observed that the concentration of HCHO reaches a plateau value after about 6 min of irradiation using UV light. The quantum yields (ϕ) for the formation of HCHO were also determined as 0.025 and 0.018 with UV light and sunlight, respectively (Table 1).

The formation of HCHO can be explained in terms of the reaction of $^{\bullet}OH$ formed from the photolysis of ferric perchlorate. The reaction of $^{\bullet}OH$ with methanol is diffusion-controlled and is reported to proceed through an H abstraction resulting in the formation of mainly hydroxymethyl radicals ($^{\bullet}CH_2OH$ ($\geq$98%)) and a small percentage of methoxyl radical ($CH_3O^{\bullet}$) [21]. However, $CH_3O^{\bullet}$ can rapidly get rearranged to $^{\bullet}CH_2OH$ [22]. $^{\bullet}CH_2OH$ belongs to

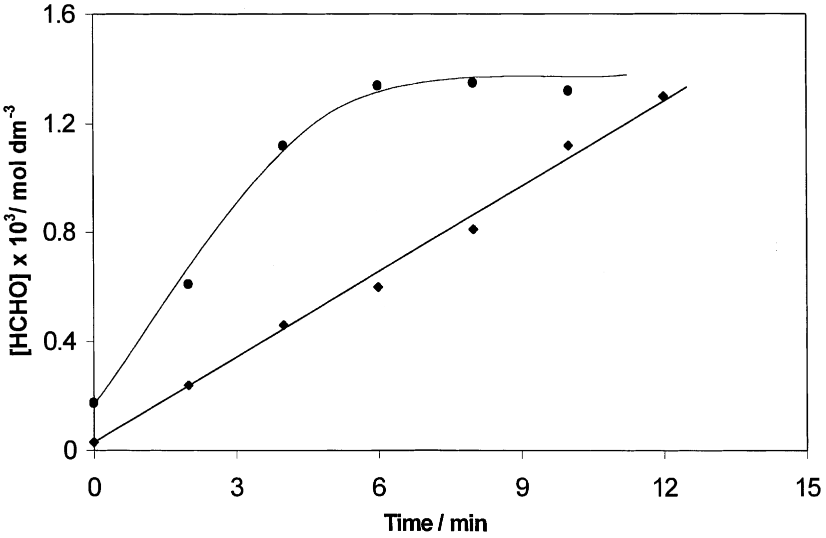

Fig. 1. Formation of HCHO as a function of time of irradiation of a solution containing ferric perchlorate (10^{-2} mol dm^{-3}) and methanol (1 mol dm^{-3}) using sunlight (◆) and UV light (●).

the class of α-hydroxyalkyl radicals which can, in general, act as reducing radicals via either electron transfer or an addition at the nucleophilic center of an organic compound. In solution state, it can also undergo a disproportionation reaction in the absence of any reactive solute. Since the reaction mixture contained both oxygen and Fe^{3+}, the second possibility (i.e., disproportionation reaction) can be ruled out if one compares the competition of $^{\bullet}CH_2OH$ between its disproportionation reaction and its reaction with O_2 and/or Fe^{3+}. As both O_2 and Fe^{3+} are highly reactive towards $^{\bullet}CH_2OH$ [21], a competition between these two reactions is expected. Assuming that in the reaction mixture, the concentration of O_2 is approximately 2×10^{-4} mol dm^{-3} (at 1 atm) and that of Fe^{3+} is 10^{-2} mol dm^{-3}, it can be seen that about 55% of the reaction of $^{\bullet}CH_2OH$ will be with O_2 and 45% with Fe^{3+} based on the second-order rate constants, $k_{(^{\bullet}CH_2OH+O_2)} = 4.9 \times 10^9$ dm^{-3} mol^{-1} s^{-1} and $k_{(^{\bullet}CH_2OH+Fe^{3+})} = 8 \times 10^7$ dm^{-3} mol^{-1} s^{-1} [21].

Table 1
The quantum yields (ϕ) of formaldehyde, phenol and TBA-RS obtained from the photolysis of ferric perchlorate (10^{-2} mol dm^{-3}) in the presence of methanol (1 mol dm^{-3}), benzene (10^{-3} mol dm^{-3}) and 2-deoxy-D-ribose (10^{-2} mol dm^{-3}), respectively, and the calculated quantum yield of $^{\bullet}OH$ at pH 2.5–3.0

Product	ϕ (product)		ϕ ($^{\bullet}OH$)$_{calculated}$[a]	
	UV	Sunlight	UV	Sunlight
HCHO	0.025	0.018	0.025	0.018
C_6H_5OH	0.0098	ND[b]	0.018	ND
TBA-RS	0.0038	0.0027	0.019	0.014

[a] These calculations are based on the percentage contribution of $^{\bullet}OH$ in the formation of each product (see text).

[b] Not determined.

Reaction of $^{\bullet}CH_2OH$ with O_2 is reported to lead to a peroxyl radical, $^{\bullet}O_2CH_2OH$, and this can give rise to HCHO and $HO_2^{\bullet}$ as shown in reactions (4)–(6) [23]. The unimolecular decay of $^{\bullet}O_2CH_2OH$ (reaction (5)) is faster in basic medium; however, no clear idea is available for the exact behavior of $^{\bullet}O_2CH_2OH$ in acidic conditions. A possible bimolecular decay was proposed by Rabani et al. [23]. On the other hand, either from reaction (5) or from the bimolecular decay, HCHO will be the end product and hence the quantitative formation of HCHO will not be affected by these different reaction mechanisms. Unlike O_2, Fe^{3+} mainly undergoes an electron transfer reaction with $^{\bullet}CH_2OH$ [21] which can yield HCHO (reactions (7) and (8)):

$$^{\bullet}OH + CH_3OH \rightarrow {}^{\bullet}CH_2OH + H_2O \quad (3)$$

$$^{\bullet}CH_2OH + O_2 \rightarrow {}^{\bullet}O_2CH_2OH \quad (4)$$

$$^{\bullet}O_2CH_2OH \rightarrow HCHO + O_2^{\bullet -} + H^+ \quad (5)$$

$$O_2^{\bullet -} + H^+ \Leftrightarrow HO_2^{\bullet} \quad (6)$$

$$^{\bullet}CH_2OH + Fe^{3+} \rightarrow {}^{+}CH_2OH + Fe^{2+} \quad (7)$$

$$^{+}CH_2OH \rightarrow HCHO + H^+ \quad (8)$$

The mechanism described in reactions (3)–(8), thus, yield HCHO as the end product. There is no report so far about the possible reaction between $HO_2^{\bullet}$ and CH_3OH/$^{\bullet}CH_2OH$, and it may not be likely that it has any meaningful reaction which can interfere with the yield of HCHO. Assuming that the reactions shown in (3)–(8) are the only possible reactions, one can expect an equivalent yield of $^{\bullet}OH$ in the reaction mixture. The quantum yield of HCHO is in line with this argument. The ϕ(HCHO) (i.e., 0.025 and 0.018 with UV light and sunlight, respectively) are also in agreement with a reported ϕ($^{\bullet}OH$) which is 0.02 [11]. Such quantitative yield

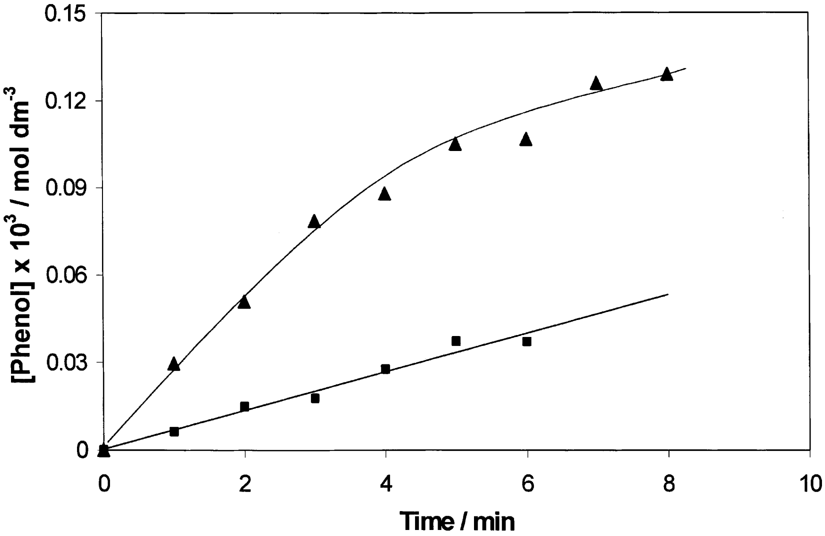

Fig. 2. Formation of phenol from the photolysis of ferric perchlorate (10^{-2} mol dm^{-3}) and benzene (10^{-3} mol dm^{-3}) using UV light in the presence (■) and absence (▲) of EDTA (10^{-3} mol dm^{-3}).

of HCHO confirms two important points: (i) $^{\bullet}$OH is the major reactive species that initiate the oxidation of methanol and (ii) both O_2 and Fe^{3+} are involved in the formation of HCHO as oxidizing agents.

Fig. 1 further shows a saturation of the concentration of HCHO after about 6 min irradiation by UV light whereas it was seen linear even after 12 min irradiation using sunlight. This can be, most likely, due to the formation of Fe^{2+} to a concentration level which can compete with Fe^{3+} for the absorption of light. It must be noted that the Fe^{2+} has absorption in the same region, though the absorption coefficient is much smaller compared to Fe^{3+}. The slightly lower yield observed in the case of sunlight irradiation may be due to the low intensity of sunlight.

3.2. Formation of phenol from benzene

Aromatic hydroxylation is one among the typical reactions of $^{\bullet}$OH and is seen used for the detection of $^{\bullet}$OH in the case of Fenton reaction [24] and of the photolysis of aqueous HNO_2 and NO_2^- [25]. The formation of phenol was monitored in a solution containing ferric perchlorate and benzene after photolysis using HPLC. The time-dependent formation of phenol is shown in Fig. 2 and a quantum yield of 0.0098 has been calculated. The formation of Fe^{2+} in the presence and absence of benzene was also investigated. The formation profile of Fe^{2+} is shown in Fig. 3. The yield of phenol has been found to be highly reduced when EDTA was added to the reaction mixture. The time-dependent for-

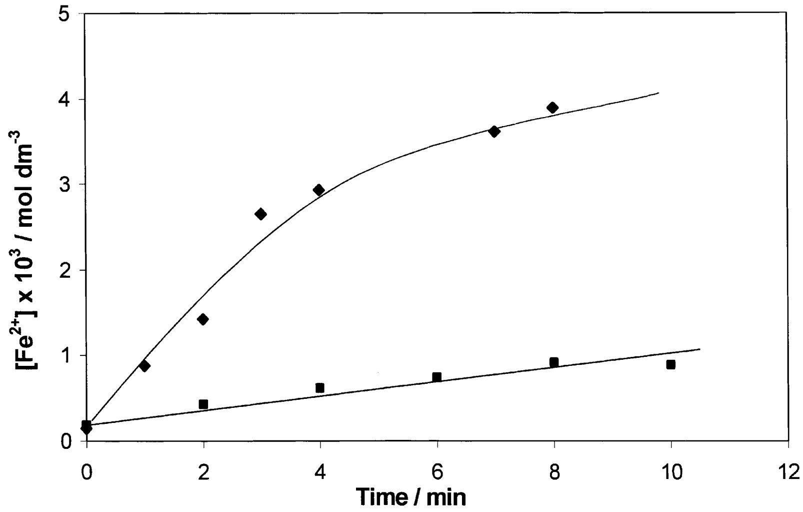

Fig. 3. Formation of ferrous ion in the photolysis of ferric perchlorate (10^{-2} mol dm^{-3}) using UV light in the presence (◆) and absence (■) of benzene (10^{-3} mol dm^{-3}).

mation of phenol in the presence of EDTA (10^{-3} mol dm^{-3}) is also shown in Fig. 2. Correspondingly, a low ϕ(phenol) as 0.0025 is calculated from this plot.

The initial attack of $^{\bullet}$OH is reported to produce a hydroxycyclohexadienyl radical with a second-order rate constant of 7.8×10^9 dm^3 mol^{-1} s^{-1} [21]. The hydroxycyclohexadienyl radical has a high affinity for O_2 ($k = 3.1 \times 10^8$ dm^3 mol^{-1} s^{-1}) [26], and can form the corresponding peroxyl radical as shown in reactions (9) and (10). Phenol is formed from this peroxyl radical after the elimination of $HO_2^{\bullet}$ [26]:

$$C_6H_6 + {}^{\bullet}OH \rightarrow C_6H_6OH^{\bullet} \qquad (9)$$

$$C_6H_6OH^{\bullet} + O_2 \rightarrow C_6H_6OHO_2^{\bullet} \qquad (10)$$

$$C_6H_6OHO_2^{\bullet} \rightarrow C_6H_5OH + HO_2^{\bullet} \qquad (11)$$

As mentioned in Section 3.1, there could be two competing reactions in the present case as well, the oxygen addition to hydroxycyclohexadienyl radical and the reaction of Fe^{3+} with hydroxycyclohexadienyl radical. Although it is reported that the presence of Fe^{3+} can enhance the yield of phenol by an electron transfer mechanism [27], the rate of such electron transfer from the hydroxycyclohexadienyl radical to Fe^{3+} has not been reported. Therefore, a quantitative distinction could not be made between the contributions of O_2 and Fe^{3+}. However, a much lower rate of reaction of Fe^{3+} with the hydroxycyclohexadienyl radical is expected compared to O_2 and therefore we assume that most of the reaction of hydroxycyclohexadienyl radical is with O_2. Furthermore, it has been demonstrated in a radiation chemical study that only about 53% of the total yield of $^{\bullet}$OH will give rise to phenol at acidic and neutral pHs and the rest will lead to a variety of other products [26].

The enhanced time-dependent formation of Fe^{2+} in the presence of benzene (Fig. 3), on the other hand, gives a strong indication that Fe^{3+} is involved in different stages of the reaction. One of the most probable among such reactions can be its interaction with $HO_2^{\bullet}$. Fe^{3+} is reported to have a high reactivity towards $HO_2^{\bullet}$ (reaction (12)) with a rate constant of 1×10^6 dm^3 mol^{-1} s^{-1} at pH 2.7 forming Fe^{2+} [28]:

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \qquad (12)$$

Although Fe^{2+} has a similar reactivity towards $HO_2^{\bullet}$ ($k = 1.2 \times 10^6$ dm^3 mol^{-1} s^{-1}) [29], whereby the Fe^{3+} can be regenerated, the dominating reaction would be the reaction of Fe^{3+} with $HO_2^{\bullet}$ as the concentration of Fe^{3+} is much higher compared to Fe^{2+}. Other than the reaction of Fe^{3+} with $HO_2^{\bullet}$, there could be more channels for the formation of Fe^{2+} such as the reaction of Fe^{3+} with the hydroxycyclohexadienyl radical (though the exact contribution is unknown) and with other intermediates resulting from the hydroxycyclohexadienylperoxyl radical since only about 53% of the hydroxycyclohexadienylperoxyl radicals will lead to the formation of phenol and the rest will contribute to different products via different intermediates, as mentioned above. Therefore, the reaction of Fe^{3+} with the possible reducing intermediates from the hydroxycyclohexadienylperoxyl radicals could also give rise to Fe^{2+}. However, a discussion on such reactions would be beyond the scope of this work, but the details of the different intermediate radicals can be obtained from Pan et al. [26]. Therefore, the time-dependent formation of Fe^{2+} in the presence and absence of benzene is used only to demonstrate the involvement of Fe^{3+} in the reaction and is not used to account for any quantitative aspect of the reaction. Further studies must be necessary to understand the involvement of Fe^{3+} as well as Fe^{2+} in various steps of the reaction. A similar enhancement of the formation of Fe^{2+} is reported in the presence of 2-chlorophenol in the photolysis of ferric perchlorate [14].

The observed hydroxylation of benzene is fully in line with the argument of the production of $^{\bullet}$OH in the ferric perchlorate system. The quantum yield of phenol is 0.0098. From the reaction mechanism described above, it is clear that only about 53% of the total yield of $^{\bullet}$OH will give rise to phenol. Hence it would be a good approximation to divide the experimentally observed quantum yield of phenol by 0.53 in order to account for the total quantum yield of $^{\bullet}$OH. In this way, a quantum yield of 0.018 is calculated which represents the total yield of $^{\bullet}$OH. This value is in agreement with the reported quantum yield [11]. Further support for the involvement of $^{\bullet}$OH has come from Fig. 2 where the yield of phenol is highly reduced when EDTA is used in the reaction mixture. As the stability constant of Fe(III)–EDTA complex is very high ($K = 1.7 \times 10^{24}$), the formation of $Fe(OH)^{2+}$ can be very well intercepted by the presence of EDTA. Such reduction in the concentration of $Fe(OH)^{2+}$ would eventually reflect the low yield of $^{\bullet}$OH. On the other hand, this reduction is not due to the reaction of $^{\bullet}$OH with EDTA since the concentration of benzene is high enough to scavenge most of the $^{\bullet}$OH with its high reaction rate constant (see above).

3.3. Formation of TBA-RS from deoxyribose in the presence of TBA

TBA assay in the presence of deoxyribose is a well-established method for the detection of $^{\bullet}$OH in aqueous medium [21]. Photolysis of ferric perchlorate in the presence of 2-deoxy-D-ribose has been carried out and the amount of TBA-RS formed was measured using TBA as mentioned in the Experimental. Similar to the formation of HCHO and phenol in the previous cases, a time-dependent formation of TBA-chr was observed using both UV light and sunlight. Recently, we have demonstrated that by selecting suitable competitors for $^{\bullet}$OH, this reaction can be utilized for determining the second-order rate constant for the reaction of $^{\bullet}$OH with a variety of biologically and environmentally important compounds [30,31]. This calculation is based on a simple competition kinetics assuming that the absorbance of the TBA-chr is proportional to the rate of formation of $^{\bullet}OH$. The quantum yields for the formation of TBA-chr were calculated using sunlight and UV light and were found to be about 0.0038 and 0.0027, respectively.

2-Deoxy-D-ribose is a well-known scavenger of $^{\bullet}OH$. The mechanism of the formation of TBA-RS (which was identified as malondialdehyde) was proposed to be by an initial attack of $^{\bullet}OH$ at the C-4 position of the deoxyribose leading to the formation of a peroxyl radical in the presence of O_2 which on subsequently give rise to malondialdehyde along with other by-products such as H_2O_2 [32]. Such an abstraction of H atom from the C-4 position of the sugar was reported using radiolytic technique under N_2O saturation where $^{\bullet}OH$ is the major reactive species [33]. Similar reaction mechanism can be considered in the present case as well, since the reaction was carried out in aerobic conditions. However, the experimentally determined ϕ values of TBA-RS are much smaller compared to the expected ϕ value (i.e., 0.02). In this context, one has to look at the reaction mechanism more closely. It is reported that the hydrogen abstraction is possible from all the carbon atoms of the sugar [33]. However, only those abstraction from the C-4 position will ultimately give rise to malondialdehyde (which is the TBA-RS) and this is found to be about 20% of the total $^{\bullet}OH$ yield [33]. We have, therefore, considered this fraction in accounting for the total quantum yield of $^{\bullet}OH$ and according to this calculation, the $\phi(^{\bullet}OH)$ were 0.019 and 0.014 using UV light and sunlight, respectively. The quantum yield (0.019) obtained with UV light is well comparable with the calculated quantum yield of $^{\bullet}OH$ from (i) and (ii) and hence it can be understood that a similar initiation of the reaction by $^{\bullet}OH$ is taking place in the photochemical formation of TBA-RS.

3.4. Hydroxyl radical production in the radiolysis of water: a comparison with the photochemical experiments

Radiolysis of water is one among the clean sources of $^{\bullet}OH$ and its production has been well established as shown in Eqs. (13) and (14) [34]:

$$H_2O \rightsquigarrow {}^{\bullet}OH,\ e_{aq}^{-},\ {}^{\bullet}H,\ H_2O_2,\ H_2,\ H^{+} \tag{13}$$

$$e_{aq}^{-} + N_2O \rightarrow {}^{\bullet}OH + OH^{-} + N_2 \tag{14}$$

The radiation chemical yield of different species is generally expressed in terms of *G*-value which is defined as the number of molecules formed or destroyed/100 eV of absorbed energy and can be converted to its SI unit by multiplying with a factor of $1.036 \times 10^{-7}\,\mathrm{mol\,J^{-1}}$. Irradiation of N_2O-saturated aqueous solutions is known to yield $^{\bullet}OH$ with *G*-values, 5.2–6.7 $\times 10^{-7}\,\mathrm{mol\,J^{-1}}$ depending on the concentration of the solute and its reaction rate constant [35].

The kinetic and mechanistic aspects of the reaction of $^{\bullet}OH$ with methanol, benzene and deoxyribose are well documented in radiation chemistry. However, in order to compare the results obtained from photochemical experiments, γ-radiolysis was carried out with N_2O-saturated aqueous solutions containing methanol ($1\,\mathrm{mol\,dm^{-3}}$) and potassium ferricyanide ($10^{-4}\,\mathrm{mol\,dm^{-3}}$) at pH 6 at different doses. A dose-dependent formation of formaldehyde (determined using acetyl acetone reagent as described in Section 2) was observed and is shown in Fig. 4. A *G*-value of $5.4 \times 10^{-7}\,\mathrm{mol\,J^{-1}}$ is determined from Fig. 4 for the formation of HCHO. Under N_2O-saturated conditions, $^{\bullet}OH$ is the major oxidizing species according to Eqs. (13) and (14). As can be seen from the *G*(HCHO) that a nearly quantitative reaction of $^{\bullet}OH$ with methanol is taking place in

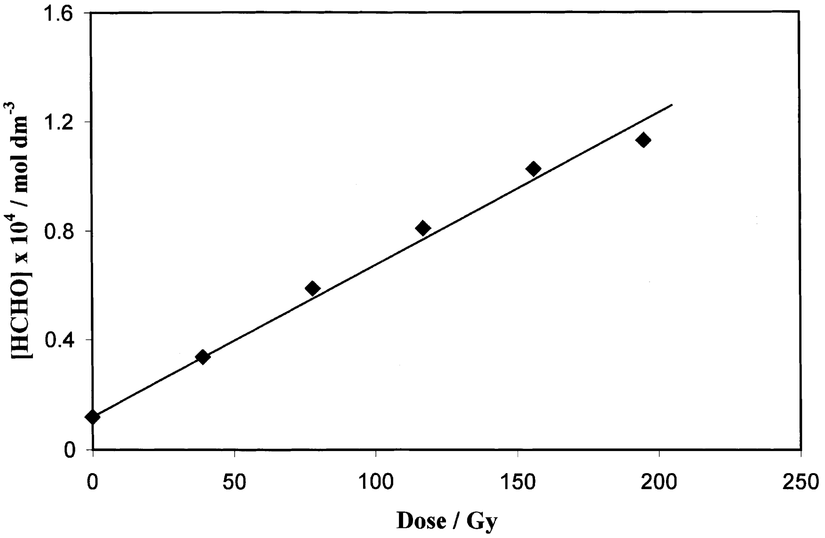

Fig. 4. Radiolytic formation of HCHO as a function of absorbed dose in a N_2O saturated aqueous solution of methanol ($1\,\mathrm{mol\,dm^{-3}}$) in the presence of potassium ferricyanide ($10^{-4}\,\mathrm{mol\,dm^{-3}}$) using ^{60}Co-γ-source.

the presence of potassium ferricyanide. The hydroxymethyl radicals (formed from reaction (3)) have a high reactivity towards ferricyanide and can easily undergo an electron transfer reaction that can lead to the formation of HCHO (reaction (15)) [36]:

$$^{\bullet}CH_2OH + Fe(CN)_6{}^{3-} \rightarrow HCHO + H^+ + Fe(CN)_6{}^{4-} \quad (15)$$

The reaction of $^{\bullet}OH$ with methanol using radiation chemical technique is well comparable with that in the ferric perchlorate photolysis system and therefore is a clear proof for the involvement of $^{\bullet}OH$ as the main oxidizing species. The mechanistic aspects of the reaction of $^{\bullet}OH$ with benzene as well as with deoxyribose using radiation chemical techniques [26,32] can be considered as clear support for the mechanisms presented in Sections 3.2 and 3.3 for the photochemical formation of phenol and TBA-RS based on the involvement of $^{\bullet}OH$. It will be also interesting to note that if the reaction proceeds the way shown in reaction (2) (see Section 1) in the case of photolysis of ferric perchlorate in the presence of benzene, the formation of phenol will be highly unlikely.

4. Conclusions

Formation of formaldehyde from methanol, phenol from benzene and TBA-RS from 2-deoxy-D-ribose are used to demonstrate the involvement of hydroxyl radicals in the photolysis of Fe(III)-hydroxy complexes. The close agreement of the quantum yields of formaldehyde, phenol and TBA-RS with that of the reported quantum yield of hydroxyl radicals is a clear support for the formation of hydroxyl radicals via the electron transfer mechanism from the ligand, OH^- to Fe(III) in the $Fe(OH)^{2+}$ (as shown in reaction (1)) and their subsequent reaction with the organic compounds in aqueous solutions. On the other hand, the present observations do not disagree with the concept of the mechanism via reaction (2), it may also be operational, but the formation of $^{\bullet}OH$ and its subsequent reaction with the organic molecules are unquestionable from the results obtained in this study. Furthermore, on the basis of the results with sunlight ($\phi(^{\bullet}OH) = 0.014$–$0.018$), it can be concluded that sunlight photolysis of ferric perchlorate is an equally efficient system for the production of hydroxyl radicals. Due to the reasonably high yield of hydroxyl radicals from the photolysis of ferric perchlorate, it is expected that this must attract a high degree of importance in the class of AOPs.

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