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Photosensitized degradation of cyclohexanol by Fe(III) species in alkaline aqueous media

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Abstract

The degradation of cyclohexanol that can be photoinduced by Fe(III) derivatives (e.g. nitrate, pyrophosphate and sulfate) has been investigated in aqueous media at room temperature and under neutral to alkaline conditions with continuous irradiation at 254, 366 and around 500 nm for 24 h. The conditions chosen are those putative to the Martian soil, and the experiments were relevant in view of the Viking experiments. The conventional homogenous photocatalytic process that is based on the reduction of Fe(III) into Fe(II) and that is responsible for the continuous production of hydroxyl radicals also occurs under the alkaline conditions used. During the oxidation of cyclohexanol, cyclohexanone was formed in reasonable amounts in the presence of the nitrate salt, while with the other two iron salts it was present in negligible amounts, and carbon dioxide was instead the dominant reaction product. Together with cyclohexanone, some unusual dihydroxylated and ketohydroxylated cyclic products were also formed. The full product distribution allows us to infer the mechanism involved: the nitrate salt produces a large amount of $HO^\bullet$ that leads to an unselective reaction pathway, with the formation of a several cyclohexyl reaction products, while with iron pyrophosphate and iron sulfate, mineralization to CO_2 is the dominant pathway, although there remains a minor conversion pathway to cyclohexanol (35% versus 85% of the aqueous cyclohexanol nitrate salt).
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1. Introduction

Among the different ways for the chemical degradation of organics, reactions producing hydroxyl radicals in aqueous solution and at low temperature are particularly attractive (advanced oxidation processes, AOPs). Hydroxyl radicals have a very high oxidation potential ($E^\circ = +2.8$ V) and they are thus capable of (unselectively) oxidizing almost all organic compounds. These radicals can be formed upon photoexcitation of iron(III), both alone and in the presence of H_2O_2 (the use of H_2O_2 as an oxidant represents the photo-Fenton process): in aqueous solutions and under UV light, low-molecular-weight Fe(III) complexes can undergo photochemical reduction to Fe(II) [1], which is then re-oxidized by oxidants (e.g. dissolved oxygen) to Fe(III), with the formation of a hydroxyl radical (Fig. 1).

Photochemical reactions of acidic iron(III) solutions (usually at pH <5) have been studied since 1949 [2] and have been widely used to achieve efficient degradation of several organic pollutants in aqueous solution [3]. In acidic media, four different well-characterized Fe(III) ions coexist in aqueous solution: $[Fe(OH)]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Fe_2(OH)_2]^{4+}$ and $[Fe(OH)_2]^+$. The dominant species is $[Fe(OH)]^{2+}$, and this has a charge-transfer band that overlaps the solar UV spectrum (290–400 nm) and that efficiently photolyzes to produce the $OH^\bullet$ radical [4]; $[Fe(H_2O)_6]^{3+}$ and $[Fe_2(OH)_2]^{4+}$ also produce $OH^\bullet$ radicals that contribute to photooxidation, although at lower levels because of their lower abundances in acidic media. There have been no reports on the photochemical properties of $[Fe(OH)_2]^+$, but it is likely that it also produces $OH^\bullet$ radicals.

Hydrolysis of Fe(III) salts gives rise to other products, which can be either soluble or insoluble, via complicated time-dependant processes [5]. Polymeric derivatives of hydrolyzed ferric salts, such as $[Fe_n(OH)_m(H_2O)_x]^{(3n-m)+}$
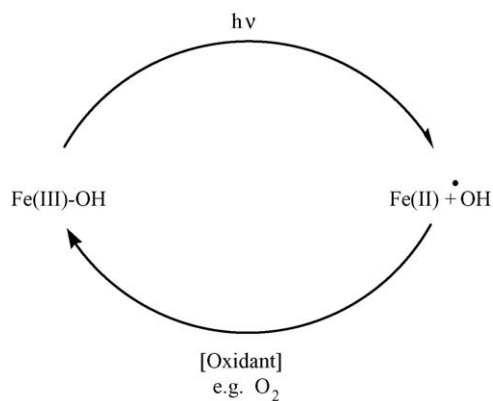
Fig. 1. Photocatalytic cycle of Fe(III) in water solution.

or $[Fe_mO_n(OH)_x]^{(3m-2n-x)}$, are the intermediate derivatives between the primary hydrolyzed products and the insoluble ones. These hydrolytic polymers are also thought to be photoreactive, as are all of their precursors, but this issue is still under debate. Finally, at higher pH, insoluble ferric oxides and hydroxides are formed, such as amorphous $Fe(OH)_3$, $FeO(OH)$ and Fe_2O_3. These have been widely studied for the photochemical oxidation of organic compounds, including α- and γ-Fe_2O_3, and α-, β- and γ-$FeO(OH)$, both in natural water and in atmospheric and surface droplets [6]. Amorphous $Fe(OH)_3$ can easily dissolve in acidic solutions to produce Fe^{3+} and Fe(III)-hydroxo complexes as the transition from the solid to the aqueous phase is faster than for other polymorphous Fe(III) oxides. Indeed, it is well accepted that aqueous photochemical reactions have an important role in natural waters, in the reductive dissolution of $Fe(OH)_3$ to Fe^{2+} and hydroxyl radicals.

Here, we present the results of an investigation into the behaviour of organic compounds dissolved in water at neutral and alkaline pH and under UVB, UVC and visible light irradiation in the presence of iron(III) salts. The chosen conditions are likely to reflect those of the Martian soil, which appears to be alkaline, and for which the abundant presence of a variety of iron minerals has been shown [7]. Moreover, the presence of a lot of UVB and UVC radiation, which is not found on the Earth, is one of the explanations used to account for the strong oxidizing properties of the Martian soil, as inferred by the Viking experiments [8].

Cyclohexanol was the model organic substrate used, the behaviour of which under oxidizing conditions has been studied extensively. A variety of catalytic reactions have also been described for the oxidation of cyclohexanol (as a well-known industrial application, cyclohexane can be oxidized to cyclohexanol and then to adipic acid, using soluble cobalt salts and oxygen in acetic acid [9]). Both soluble transition metal complexes (i.e. metal-sulfophthalocyanines [10] and metalloporphyrins [11]) and heterogeneous catalysts (i.e. Fe-phthalocyanine complexes encapsulated in Y-zeolite [12], platinum supported on active charcoal [13] and titanium silicalite-1 (TS-1) [14]) have been reported and discussed thoroughly. In all cases, cyclohexanone is the primary oxidation product, which can be further oxidized up to bicarboxylic acids and finally to carbon dioxide, depending on the strength of the oxidizing system used.

2. Materials and methods

2.1. Reagents

In a typical experiment, 15 mL of water containing cyclohexanol (at 20 and 50 mmol/L) were irradiated at 254 and 366 nm for 24 h in the presence of the iron(III) salts, which included $Fe(NO_3)_3$, $Fe_4(P_2O_7)_3$ and $Fe_2(SO_4)_3$ (at 50 and 100 mmol/L). The iron(III) salt solutions were taken to pH 7.5 or pH 9.0 by adding NaOH pellets and/or H_2SO_4 (GLP 22 CRISON pH meter at room temperature, with CRISON standard buffer calibration solutions of pH 7.0 and 9.0). A photochemical multi-ray apparatus was used, with 10 UV lamps of 15 W each. The reactions were carried out at room temperature in quartz test tubes. At the end of reactions in the photoreactor, the temperature of the reaction mixtures was 34 °C and the pH had generally changed by ±0.8 pH units. After this irradiation, the reaction mixtures were analyzed by GC, GC–MS, and ^1H and ^{13}C NMR (before the NMR analysis, the residual paramagnetic iron was removed by precipitation; see below). The solid phases were studied by FT-IR. The iron(III) salts, the organic substrates and the chromatographic and spectroscopic standards were of the highest available purities (Aldrich).

2.2. Apparatus

The photochemical multi-ray apparatus used (Helios Italquartz, Milano, Italy) consisted of an airy radiation chamber, with one carousel with two rotating disks (diameter, 194 mm). The upper disk had 27 holes punched around the circumference (hole diameter, 15 mm), while the lower one had notches that were used to contain the 27 quartz tubes. Around the carousel, at a diameter of 285 mm, there were 10 lamps of 15 W each (length 47 cm, diameter 2 cm). These lamps were fixed in a special lampholder with IP 44 protection, and they were equipped with a special aluminium reflector to increase their radiation power.

2.3. Analysis

The organic analyses were performed on aliquots withdrawn with a microsyringe from the aqueous reaction mixtures, using an HP 6890 GLC instrument equipped with FID, and a 30 mHP-5 capillary column (0.32 mm i.d.; 0.25 film thickness), with the injection port kept at 250 °C (carrier gas: He). The identity of each product was confirmed by comparisons of the fragmentation patterns of the mass spectra obtained with a mass-selective detector (MD 800, Fisons) coupled to a gas chromatograph (GC 8000 series, Fisons) operating at 70 eV in the electron ionization mode.

Some solutions were also put into sealed (rubber) quartz test tubes to measure the carbon dioxide produced. The CO_2 evolved during the reaction was entrapped by the alkaline pH in the reaction solution. Thus, to release it for capture in an aqueous solution of freshly calibrated $Ba(OH)_2$, it was necessary to add a hypothetically equivalent amount of 1 M H_2SO_4 solution. Known aliquots from this filtered solution of $Ba(OH)_2$ were then back-titrated with 0.1 N HCl.

The reactions were also followed by ^{1}H NMR on a Bruker Avance 300 MHz spectrometer equipped with a 5 mm BBO probe. Water suppression was carried out by a presaturation sequence, using a composite pulse (zgcppr Bruker sequence). A co-axial capillary tube containing a 30 mmol/L solution of 3-(trimethylsilyl)propanoic-2,2,3,3-d_4 acid sodium salt (TSP) in D_2O water was used as reference and as a lock signal. The identity and quantitation of each product were confirmed by comparisons of the positions and intensities of suitable signals after adding measured amounts of the pure compounds to the reaction mixtures. The average reproducibility of the quantitative measurements was within 5%. Before analysis by NMR, the paramagnetic iron was removed: to 1.2 mL of reaction mixture, 0.6 mL saturated $NaHCO_3$ and then 0.4 mL of 1 M $AlCl_3$ solution were added, and after 12 h of reaction the mixture was centrifuged and the precipitate removed. The solutions were also filtered (Millex LCR 0.45 μm PTFE filters) before analysis.

The FT-IR spectra were acquired on a Perkin-Elmer Spectrum 2000 equipped with an MIR source and an MIR-TDGS detector. To record the spectra, the samples were suspended in anhydrous KBr pellets, and the spectral width for all of the experiments was 5000–370 cm^{-1}.

3. Results

Neither conversion of the substrates was observed in the absence of the radiation (Table 1), nor following irradiation in the absence of the added iron (with the exception of the nitrate solutions in the UV region; see later). The slightly alkaline aqueous solutions of cyclohexanol (pH 7.5 and 9.0, at 20 and 50 mmol/L, respectively) were irradiated at 254 and 366 nm for 24 h in the presence of various iron(III) salts (at 50 and 100 mmol/L). For comparison purpose, a single experiment was performed, irradiating at pH 7.5 an aqueous cyclohexanol solution (20 mM) by a visible light source in the presence of the above-mentioned iron(III) salts at a concentration of 50 mM.

3.1. Degradation of cyclohexanol by Fe(III) nitrate photoinduction

Under these reaction conditions (water solutions at pH 7.5 and 9.0), $Fe(NO_3)_3$ immediately and quantitatively gave rise to a red-brown precipitate, while the supernatants were colourless with no changes seen in their IR and vis spectra, even after 24 h of irradiation. The $Fe(NO_3)_3$ behaved as an efficient catalyst, leading to 65–90% conversion of the cyclohexanol at 254 nm, and less than 45% at 366 nm while, when irradiating in the visible region, the conversion was negligible. This catalysis was increasingly efficient in the presence of increasing amounts of cyclohexanol (comparing iron to cyclohexanol ratios of 50:20 versus 50:50), whereas there were no appreciable differences when the iron salt concentration was doubled in the presence of the same substrate concentration. Furthermore, there were no significant differences in this conversion with pH (between 7.5 and 9.0). The cyclohexanol was converted into a number of different products, that arose from either the selective oxidation of cyclohexanol, giving cyclohexanone, 2-cyclohexenone, vari-

Table 1
Conversion (%) of cyclohexanol after irradiation of its alkaline solutions in the presence of added Fe(III) salts[a,b,c]

	pH	Cyclohexanol, mmol/L (iron salt, mmol/L)		
		20 (100)	20 (50)	50 (50)
$Fe(NO_3)_3$[d]				
No irradiation	7.5	nd	No reaction	No reaction
254 nm		85%	90%	65%
366 nm		40%	45%	30%
450–600 nm		nd	0–5%	nd
No irradiation	9.0	nd	No reaction	No reaction
254 nm		85%	85%	75%
366 nm		40%	45%	20%
$Fe_2(SO_4)_3$[d]				
No irradiation	7.5	nd	No reaction	No reaction
254 nm		30%	40%	nd
366 nm		32%	37%	25%
450–600 nm		nd	0–5%	nd
No irradiation	9.0	nd	No reaction	No reaction
254 nm		24%	35%	12%
366 nm		24%	20%	7%
$Fe_4(P_2O_7)_3$[e]				
No irradiation	7.5	nd	No reaction	No reaction
254 nm		35%	35%	11%
366 nm		35%	26%	7%
450–600 nm		nd	25%	nd
No irradiation	9	nd	No reaction	No reaction
254 nm		40%	39%	14%
366 nm		45%	45%	15%

nd: Reaction not performed.

[a] Conversion after 24 h of irradiation, without stirring and without thermostatic control (initial temperature 20 °C; final temperature 32 ± 2 °C).

[b] No reaction in the absence of iron salts after 24 h of irradiation at either 254 nm, 366 or 450–600 nm.

[c] The pH values quoted in table are the initial values (non-buffered solutions); after 24 h of irradiation, the pH generally moved by up to ±0.8 pH unit.

[d] The salt is completely insoluble and the reaction mixture appears as a colourless solution containing a brown precipitate; no changes after 24 h of irradiation.

[e] $Fe_4(P_2O_7)_3$ is entirely soluble; after 24 h of irradiation the initial orange solutions turned green, with the occasional separation of minor amounts of a whitish precipitate that is probably attributable to ferric phosphate.

ous isomers of hydroxycyclohexanone, 1,2-cyclohexanediol and 1,4-cyclohexanedione, or from deep oxidation processes, giving hexanoic, acetic and formic acids and CO_2 (the quantitative measurements of carbon dioxide were particularly difficult, in view of the long reaction times required: nevertheless, the mass balance was satisfactorily obeyed in all of these experiments; see Table 2).

3.2. Degradation of cyclohexanol by Fe(III) sulfate photoinduction

Under the same reaction conditions, $Fe_2(SO_4)_3$ gave rise to a reaction pattern that was very similar to that described above for $Fe(NO_3)_3$, except that the conversion of cyclohexanol was significantly reduced (to less than 40%), and it was not affected by the wavelength used (at least in the UV region) and was slightly lower at pH 9.0 than at pH 7.5. Upon the oxidation of

Table 2
Irradiation of alkaline solutions of cyclohexanol in the presence of added Fe(III) salts[a,b]

	Substrate conversion					
	$Fe(NO_3)_3$		$Fe_2(SO_4)_3$		$Fe_4(P_2O_7)_3$	
	85 (%)	0.340 (mmol)	35 (%)	0.140 (mmol)	39 (%)	0.156 (mmol)
Cyclohexanone	10	0.040	–	–	Trace	Trace
2-Cyclohexenone	2	0.008	2	0.008	2	0.008
Hydroxycyclohexanones	3	0.012	2	0.008	2	0.008
1,2-Cyclohexanediol	2	0.008	–	–	Trace	Trace
1,4-Cyclohexanedione	2	0.008	–	–	–	–
Hexanoic acid	5	0.020	–	–	–	–
Acetic acid[c]	11	0.120	7	0.084	6	0.072
Formic acid[d]	15	0.360	–	–	2	0.048
CO_2[d]	18	0.432	10	0.240	33	0.792
Glutaric acid[e]	6	0.029	–	–	–	–
Succinic acid[f]	6	0.036	Trace	–	–	–

[a] Yields relative to cyclohexanol, as measured by GC and/or ^{1}H NMR (for CO_2 measurements, see Section 2).
[b] Reaction conditions: 20 mL of 20 mmol/L aqueous cyclohexanol solution (equivalent to 0.4 mmol of cyclohexanol); iron salt, 50 mmol/L; pH 9.0 (initial), pH 9.0 ± 0.8 (final); 24 h of irradiation at 254 nm; 20 °C (initial), 32 ± 2 °C (final).
[c] Yields calculated overall of the potential carbons of the initial substrate divided by three.
[d] Yields calculated over all of the potential carbons of the initial substrate divided by six.
[e] Yields calculated over all of the potential carbons of the initial substrate multiplied by five and then divided by six.
[f] Yields calculated overall of the potential carbons of the initial substrate multiplied by two and then divided by three.

cyclohexanol, there was also the formation of large, although not major, amounts of CO_2 (Table 2). Visible irradiation gave only negligible transformation.

3.3. Degradation of cyclohexanol by Fe(III) pyrophosphate photoinduction

In contrast to the previous cases, $Fe_4(P_2O_7)_3$ was soluble in the neutral–alkaline conditions used for the photoreaction. After the 24 h irradiation (at all the chosen wavelengths), the initial yellow to orange solutions had turned green, which was probably due to small changes in the pH during the reaction (as indicated by independent experiments). A colourless precipitate was also formed sometimes, the FT-IR spectra of which showed a particular new band at 984 cm^{-1} that replaced that at 896 cm^{-1} from pure $Fe_4(P_2O_7)_3$. This new band fell in the region of the asymmetric stretching of the $(PO_4)^{3-}$ anion, which strongly sug-

gested that the precipitate was ferric phosphate. The ^{31}P NMR spectra of the reaction mixtures after irradiation showed the complete disappearance of the diagnostic single signal at 4.82 ppm, which was replaced by another single signal at 5.92 ppm that showed a comparable intensity. Since the observed low field shift of the NMR signal cannot be attributed to pH changes, these results indicated a quantitative transformation of $Fe_4(P_2O_7)_3$ into another phosphorated species under these irradiation conditions. The conversion of cyclohexanol was again moderate (at less than 45%), although unlike the two cases discussed above, there was an almost quantitative formation of the ultimate degradation product, CO_2 (Table 2).

3.4. Photodegradation of cyclohexanone and acetic acid

By the end of the 24 h irradiation at both 254 and 366 nm, the cyclohexanone (20 mmol/L; pH 9.0) was quantitatively

Table 3
Irradiation of alkaline solutions of cyclohexanone and acetic acid in the presence of added Fe(III) salts[a,b]

	No catalyst (%)	$Fe(NO_3)_3$ (%)	$Fe_2(SO_4)_3$ (%)	$Fe_4(P_2O_7)_3$ (%)
Cyclohexanone conversion[c]	100	100	100	66
Hexanoic acid	50	10	20	Trace
Acetic acid[d]	10	13	4	13
CO_2[e]	Trace	Trace	Trace	3
Unidentified	5	10	–	–
Acetic acid conversion	No reaction	80	56	70
CO_2[e]	–	7	7	10

[a] Yields relatively to the substrate, treasured by GC and/or ^{1}H NMR (for CO_2 measurements, see Section 2).
[b] Reaction conditions: substrate, 20 mmol/L; iron salt, 50 mmol/L; pH 9.0 (initial), pH 9.0 ± 0.8 (final); 24 h of irradiation at 254 nm; 20 °C (initial), 32 ± 2 °C (final).
[c] Same pattern obtained by irradiating at 366 nm.
[d] Yields calculated over all of the potential carbons of the initial substrate divided by three.
[e] Yields calculated over all of the potential carbons of the initial substrate divided by six.

degraded, both in the presence and the absence of the iron salts, with the formation of large amounts of hexanoic acid, acetic acid and CO_2 in all cases (Table 3). In contrast, photooxidation (at 254 nm) of acetic acid occurred only in the presence of the iron salts, with various yields (56–80%). The only detected product was CO_2, although this showed a highly unsatisfactory mass balance, which indicated either the presence of large amounts of (an) undetected species or intrinsic difficulties in measuring CO_2 in this system (Table 3).

4. Discussion

The nature of the counter anions of the iron(III) salts used proved to be the determinant for the efficiency of the reactions studied. By taking into account the number of iron atoms in these various Fe(III) salts, in the UV region the efficiency of their catalysis followed the order $Fe(NO_3)_3 \gg Fe_2(SO_4)_3 \geq Fe_4(P_2O_7)_3$, thus indicating a critical role for nitrate. The influence of the inorganic anion on the photoreactivity of the iron species is well known; Zhou et al. [18] demonstrated that the nature of the counter-anion influences the photodegradation rate following the order $NO_3^- > Cl^- = ClO_4^- > SO_4^{2-}$. In the presence of weakly coordinating anions, such as NO_3^- and ClO_4^-, the dominant ion pair remains $[FeOH]^{2+}$ [15], while with SO_4^{2-}, two competitive ion pairs ($[FeSO_4]^+$ and $[FeOH]^{2+}$) coexist, which will influence the photoreduction of Fe^{3+}, and therefore the formation of $OH^\bullet$ radicals [16]. Furthermore, the photolysis of NO_3^- in aqueous solution results in the formation of $OH^\bullet$ radicals, thus definitely affecting the oxidation of organic compounds [17]. Thus, the differences observed in the efficiencies of the catalysis of the three iron derivatives investigated can be attributed to the corresponding counter anions. $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$ gave rise to a precipitate in the reaction conditions, and $Fe(NO_3)_3$ was the most efficient here because of the ability of NO_3^- to generate $OH^\bullet$ as well. The visible light irradiation experiments confirmed our hypothesis, since the absorption spectrum of nitrate anion does not show any appreciable absorption band in the visible region and consequently the conversion of cyclohexanol is expected to fall down dramatically (Table 1). With the soluble species $Fe_4(P_2O_7)_3$, the photoreduction of Fe(III) should be expected to be dominant and indeed it was surprisingly operating also in the presence of visible light; however, the efficiency of the reaction may also depend upon the actual nature of the activator (complexes versus aqueous species) and further studies are necessary in order to elucidate the entire mechanism. There are several examples in the literature in which the photo-oxidative properties of Fe(III) complexes (e.g. with oxalate and citrate) are modulated by the organic ligands [19].

Whereas, no conversion was observed in the absence of iron, increasing the amount of the added iron (from 50 to 100 mmol/L) affected the reaction only slightly in all of the cases examined, included with the soluble pyrophosphate derivative. This would suggest a "saturation" of the activator above certain quantities. In contrast, increasing the amount of the substrate (from 20 to 50 mmol/L, always in the presence of the same amount of added iron, 50 mmol/L) constantly led to less conversion, clearly indi-

cating that the reactions were not controlled kinetically by the concentration of cyclohexanol.

Our observation that the conversion with ferric nitrate was not sensitive to pH can be easily explained by the major role played in photooxidation by nitrate ions, the concentration of which is clearly insensitive to pH. The conversion at pH 9.0 was generally less than at pH 7.5 for ferric sulfate. Indeed, since ferric sulfate is expected to be increasingly insoluble at higher pH, this strongly suggests that the dissolved iron(III)-hydroxy complexes are the true light activators. In contrast, with ferric pyrophosphate the conversion at pH 9.0 was greater at pH 7.5. In this case, it should be noted that $Fe_4(P_2O_7)_3$ owes its solubility in alkaline media to the strong complexing ability of the pyrophosphate ions on iron(III), which clearly overcomes the solubility product of iron hydroxide in the pH range under consideration. However, the presence of increasing amounts of hydroxyl ions could lead to the formation of a variety of hydroxo-pyrophosphate complexes that have different photo-reactivities. The visible spectra (and hence the colour) of the reaction mixture is indeed highly sensitive to pH, in agreement with the presence of a number of pH-sensitive species in solution.

Despite the profound differences between the sulfate and pyrophosphate systems (heterogeneous and homogeneous, respectively), the wavelength of the irradiating light did not affect the course of the photoreaction. In contrast, with iron nitrate the conversion was distinctly and constantly greater at 254 nm than at 366 nm, clearly indicating a specific sensitivity of nitrate ions for higher energy radiation, as shown by its UV spectrum.

For the $Fe(NO_3)_3$-induced photoreactions, which were often almost quantitative, we were able to identify several C6-cyclic compounds that derived directly from cyclohexanol, i.e. cyclohexanone, cyclohexenone, various hydroxycyclohexanones, 1,2-dihydroxycyclohexane and 1,4-cyclohexanedione. Cyclohexanone is the conventional product of cyclohexanol oxidation, whereas the remote C–H bonds are assumed to be similar to the (less reactive) C–H bonds of hydrocarbons (even if the inductively electron-withdrawing hydroxyl group leads to a sort of deactivation, relative to the oxidation, of the β- and γ-C–H bonds) [20]. Indeed, in the presence of a strong oxidant like chromic acid, 2-hydroxycyclohexanone, 1,2-cyclohexanedione and 2-cyclohexenone can also often be detected among the products [21]. The only study that has reported the presence of the whole family of cyclic oxidation products observed in this investigation was that of Puchkov et al., who examined the pathways of liquid phase oxidation of neat cyclohexanol with molecular oxygen at 403 K, under which conditions the oxidizing agent is an $HO_2^\bullet$ radical [22]. Along with the compounds that originated from the oxidation of cyclohexanol at position 1 (i.e. cyclohexanone), products that derived from the oxidation of the C–H bonds in the 2, 3 and 4 positions were also detected, i.e. 1,2-, 1,3- and 1,4-dihydroxycyclohexanes, 2- and 4-hydroxycyclohexanones and 2-cyclohexenone. Keeping in mind the mechanistic pathway proposed by Puchkov, we propose that in the present case cyclohexanol undergoes an attack by $OH^\bullet$ at all the positions (the selectivity of the hydroxyl radical is notoriously low). The products arising from
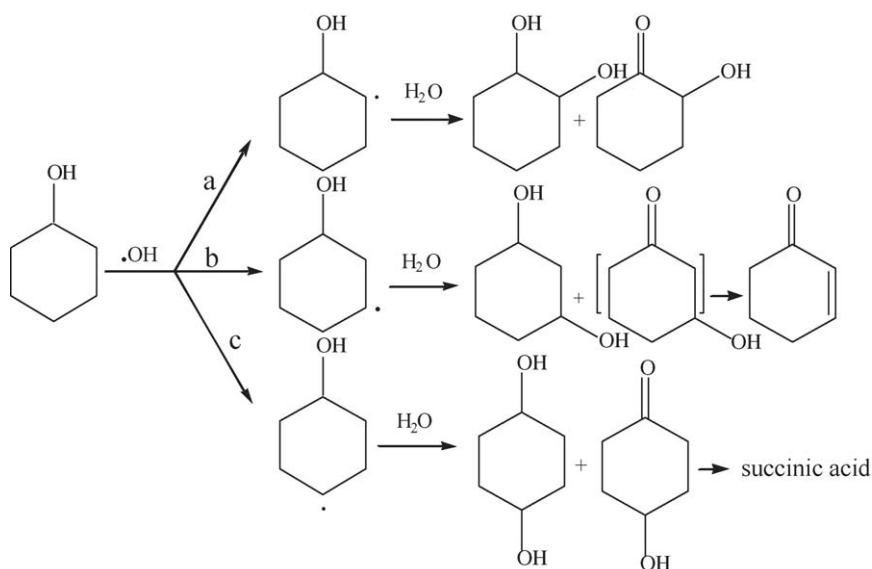
Fig. 2. Proposed reaction pathway for the formation of the dihydroxylated and ketohydroxylated reaction products observed in the presence of the nitrate salt.

the attack at the 2 and 3 positions are 2-hydroxycyclohexanone and 3-hydroxycyclohexanone, respectively, which are obtained via a dehydrogenation step (Fig. 2). Since it is well known that β-keto-alcohols are unstable under dehydration, we can assume that 3-hydroxycyclohexanone is the parent compound of 2-cyclohexenone (its formation from 2-hydroxycyclohexanone is less probable, since α-keto-alcohols are only dehydrated under severe conditions). Oxidation can also occur at position 4 (Fig. 2c), whereas the further oxidative transformations of 1,4-dihydroxycyclohexane and 4-hydroxycyclohexanone can lead to succinic acid via the "burning-out" of two carbon units; glutaric acid might be produced through a cleavage of the 1,3-cyclohexyl derivatives.

Considering the dominant formation of cyclohexanone (and the related degradation products), position 1 appears to be the most reactive one, while the different reactivities exhibited by the various iron derivatives is most likely due to the different quantities of hydroxyl radical generated in solution. In particular, when cyclohexanone is the main oxidation product (i.e. with iron pyrophosphate and sulfate), its degradation to short chain products (acetic and formic acids) and CO_2 appears to be the most probable reaction pathway.

During the oxidation of cyclohexanol in the presence of iron nitrate, hexanoic acid was also detected in the reaction mixtures. Indeed, slightly basic solutions of cyclohexanone that were irradiated at 254 and 366 nm spontaneously led to hexanoic acid even in the absence of added iron, via a hydration step on the ketene derivative that was formed by the classical Norrish I type reaction [23].

5. Conclusions

This study provides clear-cut evidence for the efficiency of cyclohexanol removal by a process of oxidative photocatalysis that can occur in neutral to alkaline aqueous media. The formation of acetic acid, formic acid and CO_2 in the reaction mixtures indicates that an efficient deep oxidation of the organics in the presence of iron(III) ions and UV light can also occur under alkaline conditions, which, to our knowledge, has never been reported previously. This finding has the possibility of being exploited in specific stages of wastewater treatment, to remove refractory organic pollutants without the addition of acid. As confirmation, a preliminary study has shown that alanine and lactic acid undergo complete oxidative degradation under the same reaction conditions (L. Garrel and M. Bressan, unpublished results). This successful procedure suggests that a similar process might have occurred in the Martian soil, during the debated Viking experiments.

References

[1] (a) W.L. Miller, D.W. King, J. Lin, D.R. Kester, Mar. Chem 50 (1995) 63–77;
      (b) B.M. Voelker, D.L. Sedlak, Mar. Chem 50 (1995) 93–102;
      (c) K. Kuma, S. Nakabayashi, K. Matsunaga, Wat. Res. 29 (1995) 1559–1569.
[2] M.G. Evans, N. Uri, Nature 164 (1949) 404.
[3] (a) See, for instance: M. Rodriguez, N. Ben Abderrazik, S. Contreras, E. Chamarro, J. Gimenez, S. Esplugas, Appl. Catal. B 37 (2002) 131–137 (and references therein);
      (b) L. Poulain, G. Mailhot, P. Wong-Wah-Chung, M. Bolte, J. Photochem. Photobiol. A: Chem. 159 (2003) 81–88 (and references therein).
[4] (a) C.J. Weschler, M.L. Mandich, T.E. Graedel, J. Geophys. Res. 91 (D4) (1986) 5189–5204;
      (b) B.C. Faust, J. Hoigné, J. Atmos. Environ. 24A (1990) 79–89;
      (c) H.J. Benkelberg, P. Warneck, J. Phys. Chem. 99 (1995) 5214–5221.
[5] C.M. Flynn Jr., Chem. Rev. 84 (1984) 31–41.
[6] M.R. Fisk, S.J. Giovannoni, J. Geophys. Res. 104 (E5) (1999) 11805–11815.

[7] G.V. Levin, P.A. Straat, Icarus 45 (1981) 494–516 (and reference therein).

[8] (a) G.V. Levin, P.A. Straat, J. Geophys. Res. 82 (1977) 4663–4667;
(b) C.P. McKay, F.J. Grunthaner, A.L. Lane, M. Herring, R.K. Bartman, A. Ksendzov, C.M. Manning, J.L. Lamb, RM. Williams, A.J. Ricco, M.A. Butler, B.C. Murray, R.C. Quinn, A.P. Zent, H.P. Klein, G.V. Levin, Planet. Space Sci. 46 (1998) 769–777.

[9] J. Kollar, US Patent No. 5 321 157, Redox Technologies Inc. (1994).

[10] N. d'Alessandro, L. Liberatore, L. Tonucci, A. Morvillo, M. Bressan, New J. Chem. 25 (2001) 1319–1324.

[11] P.A. Frey, Chem. Rev. 90 (1990) 1343–1357.

[12] F. Thibault-Starzyk, R.F. Parton, P.A. Jacobs, Stud. Surf. Sci. Catal. 84 (1994) 1419–1424 (and references therein).

[13] J.C. Bèziat, M. Besson, P. Gallezot, Appl. Catal. A 135 (1996) L7–L11.

[14] (a) G. Perego, G. Belussi, C. Corno, M. Tamarasso, F. Buonuomo, A. Esposito, Stud. Surf. Sci. Catal. 28 (1986) 129;
(b) U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinacé, E.L. Pires, Appl. Catal. A 211 (2001) 1–17.

[15] E. Rabinowitch, W.H. Stockmayer, J. Am. Chem. Soc. 64 (1942) 335–347.

[16] T.E. Graedel, M.L. Mandich, C.J. Weschler, J. Geophys. Res. D4 91 (1986) 5205–5221.

[17] (a) R.G. Zepp, J. Hoignè, H. Bader, Environ. Sci. Technol. 21 (1987) 443–450;
(b) P.L. Miller, Y.P. Chin, J. Agric. Food Chem. 50 (2002) 6758–6765.

[18] D. Zhou, F. Wu, N. Deng, Toxicol. Environ. Chem. 72 (1999) 105–111.

[19] (a) Y. Zuo, J. Hoignè, Environ. Sci. Technol. 26 (1992) 1014–1022;
(b) Y. Zuo, J. Hoignè, Atmos. Environ. 28 (1994) 1231–1239.

[20] E. Crezee, A. Barendregt, F. Kapteijn, J.A. Moulijn, Catal. Today 69 (2001) 283–290.

[21] J. Rocek, S.A. Riehl, J. Org. Chem. 32 (1967) 3569–3576.

[22] S.V. Puchkov, A.L. Perkel, E.I. Buneeva, Russian J. Appl. Chem. 75 (2002) 248–253 (and references therein).

[23] (a) G. Ciamician, P. Silber, Ber. Dtsch. Chem. Ges. 40 (1907) 2415;
(b) G. Ciamician, P. Silber, Ber. Dtsch. Chem. Ges. 41 (1908) 1071;
(c) G. Quinkert, B. Wegemund, E. Blanke, Tetrahedron Lett. (1962) 221;
(d) J.C. Dalton, K. Dawes, N.J. Turro, D.S. Weiss, J.A. Barltrop, J.C. Coyle, J. Am. Chem. Soc. 93 (1971) 7212–7221.