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Mechanistic aspects of photooxidation of polyhydroxylated molecules on metal oxides

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Abstract

Polyhydroxylated molecules, including natural carbohydrates, are known to undergo photooxidation on wide-gap transition metal oxides irradiated by ultraviolet light. In this study, we examine mechanistic aspects of this photoreaction on aqueous TiO₂, α -FeOOH, and α -Fe₂O₃ particles using electron paramagnetic resonance (EPR) spectroscopy and site-selective deuteration. We demonstrate that the carbohydrates are oxidized at sites involved in the formation of oxo-bridges between the chemisorbed carbohydrate molecule and metal ions at the oxide surface. This bridging inhibits the loss of water (which is the typical reaction of the analogous free radicals in bulk solvent) promoting instead a rearrangement that leads to elimination of the formyl radical. For natural carbohydrates, the latter reaction mainly involves carbon-1, whereas the main radical products of the oxidation are radical arising from H atom loss centered on carbon-1, -2, and -3 sites. Photoexcited TiO₂ oxidizes all of the carbohydrates and polyols, whereas α -FeOOH oxidizes some of the carbohydrates, and α -Fe₂O₃ is unreactive. These results serve as a stepping stone for understanding the photochemistry on mineral surfaces of more complex biomolecules such as nucleic acids.

1. INTRODUCTION

In this study we revisit the photooxidation of polyhydroxylated molecules (including natural carbohydrates) on wide gap metal oxides that were previously examined using transient absorption spectroscopy.^{1,2} While optical detection allowed detailed studies of photooxidation kinetics, it provided limited mechanistic understanding. The radicals derived from the carbohydrates do not have absorption bands where the oxides are transparent to probe light, so that the information about the photoreaction is inferred indirectly through observation of the light-absorbing electrons and holes on the oxide.¹ In the present study, we use matrix isolation electron paramagnetic resonance (EPR) spectroscopy to provide more direct mechanistic insights at molecular detail. Our study continues the examination of biomolecule and cellular metabolite photochemistry on mineral surfaces (previous research included amino acids and peptides).^{3,4} Carbohydrates, with ribose and 2'-deoxyribose being part of the sugar phosphate backbone of nucleic acids, serve as a stepping stone between studies of simple monatomic^{3,5} and polyatomic^{1,2,3} alcohols and complex biomolecules, such as nucleotides, oligonucleotides, RNA, and DNA.⁶ While our main motivation is

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assessing the photostability of such biomolecules on Mars aiming at identification of photochemically durable biosignatures, the impact is broader, as photoactive metal oxides, such as TiO_2 , find increasing applications in fragmentation mass spectrometry,⁷ photodynamic therapy,⁸ reforming of biomass,⁹ water treatment,¹⁰ and light-induced assembly of hybrid structures (such as TiO_2 - cyclodextrin assemblies^{11–13} and TiO_2 -cyclodextrin-carbon nanotube wires¹⁴). While iron (III) oxides are ubiquitous on earth, these oxides also frequently occur at the surface of interstellar dust grains, where these catalysts are involved in photo- and radiolytically induced redox reactions.¹⁵ On Mars, highly dispersed, iron (III) oxide rich soil (potentially harboring the organic biosignatures) is exposed to ultraviolet radiation transmitted by the thin atmosphere of this planet.^{3,4,16,17} It is not presently known what types of bioorganic molecules can survive such an exposure.^{16–18}

That polyhydroxylated molecules, such as polyvinyl alcohol, can be efficiently photooxidized by wide-gap oxides has been long recognized,¹ but only recently was it realized that the main mechanism for this oxidation involves direct, interfacial proton coupled electron transfer from a *chemisorbed* molecule to the photogenerated hole.^{1,2,11,19,20} Following this realization, this reaction became diagnostic for interfacial hole reactivity in a variety of doped and undoped metal oxide systems.²⁰ This reaction is very rapid (< 1 ns).^{1,20} The efficiency of oxidation was shown to increase dramatically with the number of vicinal hydroxyl groups in a molecule, suggesting bidentate mode of absorption at the surface.² Subsequent computational studies of Balducci¹⁹ and Du *et al.*² indicate that glucose on anatase does exhibit preference for bidentate binding that involves the formation of two $\text{Ti}^{\text{IV}}\text{-O-C}$ bridges involving the vicinal hydroxyl groups (Schemes 1 and 2). According to these *ab initio* and density functional theory (DFT) calculations, glucose is bound to two metal ions in a $\text{Ti}^{\text{IV}}(\mu\text{-O}_2)\text{Ti}^{\text{IV}}$ surface group forming a surface complex with the net charge of -2 . The dissociative adsorption (that results in the formation of a ~ 0.18 nm Ti-O bond) competes with molecular adsorption in which the oxygens in the hydroxyl groups of the glucose form bonds with the Ti^{IV} atoms, which are ~ 0.23 nm; the resulting surface complex is neutral. The calculated energies for molecular bridge adsorption on a dry (101) anatase surface are ~ 0.3 eV higher than the energy for the dissociative bridge absorption; the latter energies increase from 0.4 eV for $\text{O}(1)\text{-O}(2)$ to 0.5–0.6 eV for $\text{O}(2)\text{-O}(3)$ and $\text{O}(3)\text{-O}(4)$ to 1 eV for $\text{O}(4)\text{-O}(6)$ (see Scheme 1 for the atom numbering). However, these calculations do not take into account water around and at the surface, which can drastically weaken the molecular adsorption at the surface. EPR studies on the photooxidation of methanol^{3,5} and other monohydric compounds³ indicate that the radical product is the $\text{Ti}^{\text{IV}}\text{-O-CRR}^\bullet$ radical (as opposed to the $\text{Ti}^{\text{IV}}\text{...O(H)CRR}^\bullet$) suggesting that the *photooxidation involves primarily the molecules that are chemisorbed in a dissociative fashion*.

In the latter case, the calculations indicate that regardless of the particular hydroxyl groups involved, the highest occupied molecular orbital of the surface complex is always localized on the bridging oxygens, which accounts for the ease of the photooxidation.^{12,19} By contrast, molecular adsorption of glucose does not localize the hole on these oxygens in configurations other than those involving the $\text{O}(3)\text{-O}(4)$ atoms.¹⁹ The radical cation generated by the interfacial charge transfer promptly loses the proton to the solvent or the oxide surface (most likely in a concerted fashion with the charge transfer) thereby forming the corresponding C-centered H atom loss radical.^{1–5} For monohydric molecules, these $\text{Ti}^{\text{IV}}\text{-O-C}^\bullet$ radicals can inject the electron into the oxide surface forming a bound $\text{Ti}^{\text{IV}}\text{...O=C}^\bullet$ complex with the net charge of -1 ;^{1,12} this reaction is believed to be the main channel for radical decay on the oxides and the C=O stretch of the ketone can be directly observed using time-resolved infrared spectroscopy.¹ As this $\text{Ti-O-C}^\bullet$ radical can also serve as a hole trap, further oxidation produces $\text{TiO-C(R)=C(R')-OTi}$ and $\text{Ti...O=C(R)-C(R')=O...Ti}$ species,

where R and R' are the substituting groups.¹² The stretching modes of the C=C and C=O bonds have been observed in photoirradiated TiO₂-cyclodextrin solutions.¹¹

These chemical transformations are quite different from the more familiar radical chemistry of polyhydroxylated molecules in bulk aqueous solutions and glasses^{21,22} and single crystals.²³ Under acidic condition, free radicals of the $\cdot\text{C}_\alpha(\text{R})\text{OH}-\text{C}_\beta\text{H}(\text{R}')\text{OH}$ -type readily dehydrate via reaction (1) as shown in Scheme 2.21 This reaction occurs in three steps.²² First, the β -hydroxyl group is protonated and the resulting radical cation reversibly eliminates water. This intermediate radical cation is unstable, rapidly eliminating the proton from the α -hydroxyl group and undergoing 1,2-shift, yielding the secondary $\text{-C}_\alpha(\text{R})(=\text{O})\text{-C}_\beta\text{H}(\text{R})\cdot$ radical. Typically, in experiments that are not carried out in a time-resolved fashion,²² only such radicals are observed.²¹ These secondary radicals abstract hydrogen from the parent molecule, yielding the corresponding deoxy-compounds. Below we demonstrate that this textbook reaction does not occur on metal oxides; the reaction mechanism is indeed different.

For brevity, some tables and figures are supplied as supporting information; such materials have the designator "S" (as in Fig. 1S).

2. EXPERIMENTAL

Unless stated otherwise, all chemicals were obtained from Sigma Aldrich and used without further purification. Deuterated sugars were obtained from Santa Cruz Biotechnology, Inc. and Omicron Biochemicals, Inc. Aqueous anatase nanoparticles and ferric oxide microparticles were synthesized as described in ref. 3. The aqueous solutions/suspensions were irradiated using 6 ns laser pulses from the third harmonic (355 nm) of a Nd:YAG laser (Quantel Brilliant). N₂-purged solutions were flash frozen at 77 K in 4 mm Suprasil tubes and subsequently irradiated using 355 nm light (15 mJ/pulse, 100–500 pulses) while immersed in liquid N₂. The irradiated samples were transferred into the cryostat (Oxford Instruments model CF935) of a continuous-wave EPR spectrometer (Bruker model ESP300E operating at 9.45 GHz), and the radicals and spin centers on the metal oxides were detected *in situ* at 50–200 K. First-derivative EPR spectra were recorded at several temperatures, microwave power levels (typically, 0.2 mW), and field modulation amplitudes (typically 2–5 G) at 100 KHz. Radicals on the oxide surface exhibit hindered rotation that results in poor averaging of the anisotropic part of hyperfine coupling tensors (hfcc) for the protons, which complicates structural attribution. Calculations of the geometric and magnetic parameters for the radicals were carried out using DFT with a B3LYP functional²⁴ and 6–31G(d,p) basis set²⁵ with polarization functions from Gaussian 98.²⁶ The computed hfcc tensors for the optimized geometry (or, in some cases, constrained geometry) radicals were used to calculate powder EPR spectra using first-order perturbation theory. Spherical *g*-tensor and Gaussian spectral envelope for resonance lines (having the same width across the entire spectrum) were assumed in these calculations and no motional averaging was taken into account.

3. RESULTS AND DISCUSSION

3.1. Polyols and carbohydrates: arrested dehydration

EPR spectra observed in photoilluminated solutions of TiO₂ containing ethylene glycol and glycerol are shown in Figure 1. The low-field sharp line indicated by an arrow in the plot is the low field component of the formyl radical (HCO[•], see Section 3.2). The lattice-trapped electrons exhibit a sharp resonance line at *g*=1.97 with the additional components to the high field (as the *g*-tensor of the lattice electrons is highly anisotropic) that overlap with a broad *g*=1.93 resonance from surface trapped electron (that is, Ti^{III} ions).^{3,4,27} The resonance

lines on the low field side of the $g=1.97$ line (from lattice-trapped electron in TiO_2) arise from the H loss radicals of the organic molecules. The appearance of this radical is similar to the one observed in radiolysis of frozen aqueous ethylene glycol after photobleaching of the trapped electron.²⁸ The latter EPR spectra were accounted for by contributions from 1,2-dihydroxyethyl superimposed on the singlet resonance line from $\text{HOCH}_2\text{CH}_2\text{O}^\bullet$ radicals. The latter attribution seems unlikely in the present system in the view of high reactivity of such O-centered radicals and the stability of the observed pattern upon sample warming. We proceed to demonstrate spectra can be explained by slow conformational dynamics of bound radical and matrix effects resulting in favored conformations that are different from free radicals.

Photoexcitation of the surface complex involving ethylene glycol is expected to produce a bound $\text{Ti}^{\text{IV}}\text{OC}^\bullet(\text{H})\text{CH}_2\text{O}^{\text{IV}}\text{Ti}$ radical shown in Figure 1S in the Supplement. In the resulting structure, the dihedral O-C-C-O angle ϕ tends to be close to 60° – 110° , as such conformations minimize binding strain. In Figure 2S, we plotted the conformational energy and isotropic hyperfine coupling constants $a(^1\text{H})$ (hfcc's) for α - and β - protons in a free radical. In these calculations all degrees of freedom were optimized with exception of angle ϕ . The minimal energy corresponds to $\phi \approx 83^\circ$, at which $a(^1\text{H}_\beta) \approx 5$ G, while $a(^1\text{H}_\alpha) \approx -15$ G. Assuming that the conformational dynamics is inhibited by the matrix, the EPR spectra of the ensemble of radicals can be obtained by Boltzmann weighing of different conformers. The low-temperature EPR spectrum is a doublet (Figure 3S). As the temperature increases (see the weight distribution plotted at the top of Figure 2S), the ensemble-average EPR spectrum indicates the additional structure resulting from the conformers with smaller or larger angles ϕ . As shown in Figure 3S, the resulting spectrum resembles the one obtained for $\phi \approx 60^\circ$. While these simulations are necessarily approximate (as the radical interacts with the surface and the solvent) the import of these calculations is that if the surface binding favors smaller torsion angles corresponding to gauche conformation in the surface complex (Figure 1S), the spectrum will exhibit the additional structure that is not observed for $\phi \approx 90^\circ$ conformers that have the lowest energy in the gas phase. This point is illustrated in Figure 4S, where we superimposed the experimental spectrum from Figure 1 with the simulated spectrum of the $\phi \approx 60^\circ$ conformer from Figure 3S. For comparison, we also showed the simulated spectrum of the $^\bullet\text{CH}_2\text{CHO}$ radical, which is the product of dehydration reaction (1) in Scheme 2. While the peak positions of the latter radical (but not its overall shape) are close to the ones in the experimental spectrum, it is seen that the latter can be accounted by the 1,2-dihydroxyethyl radical alone. This comparison suggests that the spectrum shown in Figure 4S is likely to originate from the H atom loss radical alone.

Two other considerations suggest that dehydration did not occur. In bulk solution, the $^\bullet\text{CH}_2\text{CHO}$ radical readily abstracts hydrogen from ethylene glycol. Weakly bound $^\bullet\text{CH}_2\text{CHO}$ radicals should be reactive towards the parent molecule (in our previous experiments, we observed significant decay of $^\bullet\text{CH}_2\text{CO}_2^-$ and $^\bullet\text{CH}_2\text{NH}_3^+$ radicals that are structurally similar to the $^\bullet\text{CH}_2\text{CHO}$ radical).^{3,4} Contrary to these expectations, no evolution of the spectral shape for the sample in Figure 1 was observed between 50 and 180 K (at which the matrix softens and all photogenerated radicals decay). This argues against the presence of the $^\bullet\text{CH}_2\text{CHO}$ radical. Furthermore, it is known that photoexcited $^\bullet\text{CH}_2\text{CHO}$ radical eliminates CO yielding methyl.^{22,29} Even prolonged UV irradiation of ethylene glycol on TiO_2 did not result in the appearance of the quartet of the resonance lines from the methyl radical (which we previously generated on TiO_2 by photooxidation of the acetate).³ These indirect observations also argue against the occurrence of reaction (1).

The partially resolved structure of the EPR spectrum for H atom loss radicals in Figures 1 and 5S is not observed for longer-chain polyols, such as *meso*-erythritol (C_4), D-arabitol (C_5), and D-mannitol (C_6) (structures **1**, **2**, and **3** in Scheme 1) but these compounds yield

very similar EPR spectra, suggesting that the same interior radicals are generated in all of these cases (i.e., these radicals are magnetically equivalent, due to the conformational dynamics of the open chains). On the other hand, the cyclization of the carbon chain in *myo*-inositol results in a fixed, rigid structure with nonequivalence of these β -hydrogens in the chair form of the ring, restoring the complexity to the EPR spectrum (Figure 6S). Qualitatively, the β -hydrogens have differing hfcc's for the three types of H atom loss radicals (with these protons in an axial [*a*] or equatorial [*e*] position), viz. [*aa*]: Two large proton hfcc's ~30–40 G; [*ae*]: one large hfcc and one ≈ 0 ; and [*ee*]: finally a third radical with two proton hfcc's near zero.³⁰ A composite of spectra from these differing radical sites explains the observed EPR spectrum.

Turning to natural carbohydrates, we first observe that conformational variation has little effect on the EPR spectra observed (Figure 2). For example, the spectra of D-glucose and D-galactose (structures **4** and **5** in Scheme 1) are very similar, despite the OH group at C(4) being positioned below and above the ring, respectively. In turn, these two EPR spectra are similar to the EPR spectrum observed for D-fructose (structure **6**). However, when the D-glucal (structure **7**) is used instead of D-glucose (**4**), the EPR spectrum changes considerably and the formyl signature is suppressed. As suggested by simulations of EPR spectra from the corresponding radicals in Figure 7S, the EPR spectrum for the D-glucal can be understood in terms of the overlapping spectra from $\cdot\text{C}(1)/\cdot\text{C}(2)$ and $\cdot\text{C}(3)/\cdot\text{C}(4)$ radicals.

3.2. The formyl radical

While our studies suggest that H atom loss radicals generated at the oxide surface do not dehydrate, in almost all of the systems examined, there is a prominent resonance line of the formyl radical. This fragmentation appears to be a very general photoreaction of *polyhydroxylated* compounds, both linear and cyclic, and the formyl radical is observed in many classes of such molecules and their derivatives,⁶ whereas UVA photon induced generation of the formyl radical has never been observed for alcohols with one OH group and 1,3-diols on metal oxides.^{3,4,5} The formation of the formyl from the terminal $\cdot\text{CH}(\text{OH})\text{CH}_2(\text{OH})$ - carbohydrate radical has been reported in bulk solutions.²⁸ We suggest that this type of elimination occurs much more readily on metal oxide surfaces and it involves not only terminal but also interior radicals. Therefore, we suggest that the fragmentation suggested in ref. 31 (the last step of reaction (2)) is preceded by a 1,2-shift of a pendant group shown in Scheme 2.

A possible rationale for the observed behavior is the occurrence of bidentate binding at the surface (Scheme 2). Reaction (1) involves deprotonation from the α -hydroxyl group of the intermediate radical cation and the formation of the C=O group. This step cannot occur for the bridged molecule without breaking the metal-oxygen bond. While the formation of the $>\text{C}=\text{O}$ molecules is known to occur in this fashion, it involves electron injection into the oxide with the loss of unpaired electron density.^{1,12} For this reason, the deprotonation (which is a crucial part of reaction (1)) can only occur after hydrolysis which is prohibitively slow as compared to rehydration of the intermediate radical cation. The rearrangement of pendant groups in reaction (2) provides the only possibility for the internal relaxation of the torsion strain in a surface complex. Another important consideration is that inefficiency of rearrangement reaction (2) in the bulk solutions can be the consequence of the efficiency of dehydration reaction (1) that shortens the lifetime of the H atom loss radical. As the stability of the parent radical is increased on the oxide surface, some of these radicals can undergo the rearrangement.

For cyclic carbohydrates, the rearrangement of pendant groups postulated in Scheme 2 would contract the carbohydrate ring unless the eliminated formyl originates from carbon-1. In the latter case, an open-chain radical is formed as a result of the hemiacetal/hemiketal

dissociation; in all other cases, the contractions of the ring would result in a cyclic, strained molecule, which is less energetically favored. Such open-chain radicals have been observed in irradiated single crystals of carbohydrates.³² A closer examination of Figure 2 indicates that the relative yield of the formyl radical is greatly reduced in D-fructose **6**, for which the C(1) hydroxyl is absent. This C(1) hydroxyl group is also absent in D-glucal **7** that also yield very little formyl (Figure 2). We conclude that the formyl radical mainly originates from carbon-1 fragmentation, in agreement with the mechanism shown in Scheme 2. Further proof of this preference is given by the isotope substitution experiments examined in the next section.

3.3. Isotope substitution studies of D-ribose

Figure 8S(a) exhibits the EPR spectra of D-ribose (structure **8** in Scheme 1) at various temperatures. As in other polyhydroxyl systems examined, the EPR spectrum does not evolve between 50 and 160 K suggesting the relative stability of the progenitor radicals; there is no indication of reaction (1) occurring in this system. To obtain further insight, we irradiated several isotopomers of the ribose that were selectively deuterated at 1, 2, 3, 4, and 5,5'-positions on the furanose ring (see Figure 3 and Scheme 3). The deuteron, which is a spin-1 nucleus, has ~15% of the magnetic moment of the (spin-1/2) proton and, to a first approximation, the effect of such deuteration is nullifying the hfcc in the corresponding protons. As only the hfcc's in the α - and β -protons (with regard to the unpaired electron in an hydrogen atom loss (-H) radical) need be considered, using the isotopomers allowed us to make informed guesses concerning the nature of the radicals present on the TiO₂. The corresponding radicals are labeled $\bullet$ C(1) to $\bullet$ C(5), as shown in Scheme 3; the corresponding radical products of reaction (1) have the index "d", such as $\bullet$ C_d(1). We use the convention where the prefix d_n - indicates H/D substitution in the ring proton at the C(*n*) carbon of ribose (*n*=1–5). Computer simulated powder EPR spectra for the corresponding radicals using the hfcc tensors obtained from DFT calculations are shown in Figure 9S.

Our first observation is that the formyl radical is present in the EPR spectra from all of the isotopomers with the exception of d_1 -ribose in D₂O (trace (i) in Figure 3). This suggests that the formyl radicals originate mainly from the carbon-1 site (as the DCO $\bullet$ radical does not yield the side line whose standalone location is due to the large hfcc in the single proton). If reaction (2) is the correct mechanism (Section 3.2), then (i) the $\bullet$ C(2) radical (before it rearranges) should be the main progenitor of the formyl radical and (ii) at least some of the D-ribose molecules must be bound to the TiO₂ surface through their O(1)–O(2) groups.

The formation of the $\bullet$ C(1) and $\bullet$ C(2) radicals are also suggested by the fact that d_1 - and d_2 -substitutions (traces (i) and (vi) in Figure 3, respectively) have the largest effect on the EPR spectra shown in Figure 3, whereas d_3 -substitution (trace (ii)) has a much smaller effect, and d_4 - and $d_{5,5'}$ -substitutions have very little effect (traces (iv) and (v)). The latter argues against the large contribution from $\bullet$ C(5) radicals to the composite spectrum, as $\bullet$ C(5) radicals have an anisotropic ~20 G hyperfine coupling from its H $_{\alpha}$ proton as well as a β -proton coupling from carbon-4 which would result in a significant change on deuteration at carbon-5 which is not observed. (Figure 9S). The d_1 -substitution can only affect the EPR spectrum from the $\bullet$ C(2). The DFT simulations shown in Figure 9S suggest that the effect of this d_1 -substitution should be collapsing the doublet of the $\bullet$ C(2) to a multiplet of closely spaced lines from d_1 - $\bullet$ C(2). These additional splittings are observed as "ripples" in trace (i) (Figure 3). We conclude that the $\bullet$ C(2) radicals are present in the reaction mixture.

The largest effect on the EPR spectrum is by d_2 -substitution which immediately suggests the involvement of the $\bullet$ C(1) and/or $\bullet$ C(3) radicals. As shown in Figure 9S, d_2 -substitution in $\bullet$ C(3) does not cause the collapse of its resonance lines to a singlet observed in trace (vi); rather the spectrum collapses to a doublet, whereas the d_2 -substitution in the $\bullet$ C(1) radical

collapses the corresponding spectrum to a singlet as is found experimentally. As this d_2 -substitution obviously cannot change the spectrum of the $\bullet\text{C}(2)$ radical (as the deuteron is abstracted), the spectrum for the d_2 -ribose shown in Figure 3, trace (v) can be interpreted as the superposition of contributions from the d_2 - $\bullet\text{C}(1)$ and $\bullet\text{C}(2)$ radicals, with a possible contribution from the d_2 - $\bullet\text{C}(3)$ radical. It follows from the simulations in Figure 9S that for the $\bullet\text{C}(2)$ radical, the d_3 -substitution collapses the spectrum to a singlet, while this substitution has no effect on the spectra from the $\bullet\text{C}(1)$ and $\bullet\text{C}(3)$ radicals. The simulations shown in Figure 9S suggest that the weak line indicated by open squares in Figure 3 could be from the $\bullet\text{C}(3)$ or $\bullet\text{C}(5)$ radicals. The corresponding EPR spectrum in Figure 3 for the d_3 -substituted D-ribose, trace (ii), exhibits the low field line of the $\bullet\text{C}(3)$ radical (open circle) while the feature indicated with the open square is suppressed. This feature can only be from the $\bullet\text{C}(2)$ radical. The yield of the $\bullet\text{C}(3)$ radical must be relatively low as suggested by the magnitude of the side lines and the fact that d_4 -substitution does not have strong effect on the EPR spectrum.

This examination suggests that the EPR spectrum observed from the photooxidized D-ribose is mainly from the $\bullet\text{C}(1)$, $\bullet\text{C}(2)$, and $\bullet\text{C}(3)$ radicals. Given that, one would expect that D-2-deoxyribose (structure **9** in Scheme 2) yields a rather different EPR spectrum from the D-ribose because in all three of the resulting radicals the unpaired electron is coupled to an extra proton at carbon-2. This conclusion is supported by EPR spectra shown in Figures 2 and 4: the occurrence of this extra coupling is apparent from the spectrum. As shown in Figure 4, $d_{5,5'}$ -substitution results in almost no change, which is consistent with the low yield of $\bullet\text{C}(4)$ and $\bullet\text{C}(5)$. The simulations shown in Figure 10S strongly suggest that the spectrum is a juxtaposition of the resonance lines from the $\bullet\text{C}(1-3)$ radicals, as is also the case for the D-ribose.

Given the low yield of the $\bullet\text{C}(5)$ radicals, the substitution of the 5-hydroxyl group for the phosphate group in D-ribose-5-monophosphate (structure **10** in Scheme 1) is not expected to result in drastic changes to the EPR spectrum, which is in full agreement with experiment. As in other carbohydrate systems, the EPR spectra for ribose-5-phosphate obtained between 50 and 180 K did not change (Figure 8S(b)), except for the decay of the formyl radical > 160 K, i.e. the -H radicals generated by the photocatalytic oxidation of the carbohydrates at 77 K were stable on the oxides. This is in contrast to bulk solutions, where such radicals tend to dehydrate rapidly, even at a low temperature.^{21,22}

In addition to the anatase nanoparticles, we have studied the photooxidation on hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$) microparticles. While TiO_2 binds and oxidizes all of the carbohydrates, the iron oxides are *selective* in their photochemical behavior. For hematite, no evidence for photooxidation of the carbohydrates was obtained: the only spin centers that are observed are in the oxide^{3,4} and the EPR signals do not change upon H/D substitution in the organic substrate. On the other hand, the goethite was an efficient photocatalyst for the carbohydrates (Figures 11S to 13S), but the binding constants must vary greatly with structure, as the photooxidation is very selective. As shown in Figure 11S, the photooxidation was observed for D-glucose, D-fructose, D-ribose and D-ribose-5-phosphate (which can be demonstrated through d_2 -substitution, as shown in Figure 12S). On the other hand, no oxidation was observed for D-2-deoxyribose, even at high concentration of the latter (> 0.4 M). This and other^{6,33} results indicate weaker surface binding for ribose upon 2-deoxy modification. As in the case of TiO_2 , there is no spectral evolution of ribose-related EPR spectra as a function of temperature (Figure 13S).

4. CONCLUSION

Summarizing our observations, photoirradiated TiO₂ and α -FeOOH oxides readily oxidize D-ribose (and other carbohydrates and polyhydric alcohols) and ribose-5-phosphate, as well as the corresponding 2-deoxy compounds. Overall, the photochemistry is oxidative and the primary radical products (H loss radicals) are similar to those observed in bulk solutions containing strongly oxidizing radicals, but without the complications due to electron scavenging and H and OH adduct formation. The resulting H loss radicals appear to be more stable on the oxide surfaces than in the bulk due to the inhibition of reaction (1). Our EPR studies did not provide evidence for this reaction occurring in the pH region of the colloid stability for the oxide particles below 160–180 K. Another important difference from the bulk solution is site specificity of the carbohydrate oxidation that we explain through the preferential dissociative adsorption involving the O(1)–O(2) and O(2)–O(3) oxygens. Such preference has also been suggested by the recent calculations of Balducci.¹⁹ For D-ribose, the prevalent H atom loss radicals are [•]C(1–3); the same sites yield such radicals for 2-deoxy-D-ribose. The fragmentation that occurs instead of the dehydration on these oxides is elimination of the formyl radical. For cyclic carbohydrates, this reaction involves mainly carbon-1 and we surmise that it proceeds from a carbon-2 centered radical.

The implications of these results for photooxidation of nucleotides, nucleosides and nucleic acids on metal oxides are discussed elsewhere.⁶ As shown therein, substituting carbon-1 by purines diverts the locus of charge transfer from the sugar(-phosphate) to the nucleobase, although some oxidation of the ribose still occurs. For pyrimidines other than thymine, the primary locus of the oxidative damage remains to be the ribose and 2-deoxyribose.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

First-derivative X-band EPR spectra from ethylene glycol (solid line) and glycerol (dashed line) on aqueous anatase nanoparticles (355 nm laser irradiation at 77 K). These spectra were obtained at 50 K with a modulation field of 5 G at a modulation frequency of 100 kHz; the microwave power is 2 mW. The low-field line from lattice trapped electrons is not shown; the broad line in the high field is from surface trapped electrons. The arrow indicates a feature arising from the formyl radical.

EPR signal, 1st derivative

Figure 2.

EPR spectra of photoirradiated aqueous solutions of TiO_2 nanoparticles containing various carbohydrates. The first derivative EPR spectra were obtained at 50 K, using a field modulation of 2 G (100 kHz). The structures of the carbohydrates (see the plot legend) are given in Scheme 1; the numbering corresponds to that used in the text and Scheme 1. The arrow indicates the line of the formyl radical. The part of the spectrum where lines from organic radicals overlap with lines from lattice and trapped electrons is excluded from the plot.

Figure 3.

EPR spectra of photoirradiated D-ribose isotopomers on TiO_2 in D_2O . The dotted line corresponds to protiated D-ribose in $\text{TiO}/\text{H}_2\text{O}$; the site of H/D exchange is indicated in the plot labels. The numbering scheme is given in the structure inset at the top left and Scheme 1. The vertical arrow indicates the line of the formyl radical. The dash-dot vertical lines indicate features from $\bullet\text{C}(3)$ radicals (*open circle*) and $\bullet\text{C}(2)$ radicals (*open square*), as explained in the text. The short solid vertical lines in trace (i) indicate the fine structure arising from the $d_1\text{-}\bullet\text{C}(2)$ radical. See Figure 9S for simulations of EPR spectra from the individual radicals.

Figure 4.

A comparison of EPR spectra for 5,5'-protiated and deuterated forms of 2-deoxy-D-ribose on photoirradiated TiO_2 .

Scheme 1.
Structural formulas for polyols and carbohydrates.

Scheme 2.

Possible reaction mechanisms accounting for the observed preference of reaction (2) on the metal oxide surface over reaction (1) that typically occurs in the bulk.

Scheme 3.

Structural formulas for ribose-derived $\cdot\text{H}$ radicals ($\bullet\text{C}(1-5)$) and some of the secondary radicals ($\bullet\text{Cd}(1-3)$) formed via acid-catalyzed dehydration of the primary radicals.