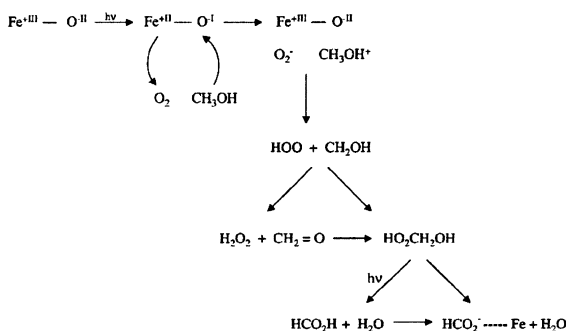


Figure 7. (a) Step-scan FT-IR spectrum of CH₃OH + O₂ photoreaction in a FAPO-5 sieve at 250 K (co-addition of 100 5 μ s time slices). (b) Identical experiment for CH₃OH + N₂ system. The insert shows the difference of traces a and b.

SCHEME 1



and does not exhibit a distinct induction period. This implies that HO₂CH₂OH, the precursor, is formed on a fast time scale compared to the rise of formate (4 s), consistent with the detection of hydroxymethylhydroperoxide within a fraction of a millisecond following CH₃OH + O₂ photolysis. Hence, the HO₂CH₂OH intermediate is most probably formed by direct coupling of HOO and CH₂OH radicals rather than reaction of CH₂=O + H₂O₂, which takes 2.6 s (250 K). Scheme 1 describes the proposed mechanism. Absorption of a photon by the Fe^{+III}–O^{II} → Fe^{+II}–O^{·-} LMCT transition results in a transiently reduced Fe center and a hole on a framework oxygen. The initial electron-transfer steps are reduction of O₂ by Fe^{+II} to O₂^{·-} and concurrent oxidation of CH₃OH by the electron-deficient framework O to the alcohol radical cation. The highly acidic CH₃OH⁺ is expected to undergo proton transfer to superoxide to form HOO and CH₂OH radicals. The latter is unstable relative to CH₂O, and isomerization of CH₃O to CH₂OH is known to proceed extremely fast.^{13–15} In the gas or solution phase, the coupling of HOO and CH₂OH radicals is close to diffusion controlled.^{16,17} The resulting two-electron-transfer product, HO₂–CH₂OH, rearranges spontaneously to HCO₂⁻···Fe and H₂O, the products observed previously by static FT-IR spectroscopy¹. Hence, the overall chemistry is a single photon-induced four-electron-transfer process with HO₂CH₂OH as the main closed-shell intermediate. Thermal disproportionation of hydroxymethylhydroperoxide to formate and H₂O in the case of the photochemical CH₃OH + O₂ system is much faster than for

authentic samples of HO₂CH₂OH or HO₂CD₂OH loaded into the sieve, or synthesized in situ by co-loading of H₂O₂ and CH₂=O.² We attribute this to the fact that photochemically produced HO₂CH₂OH is generated at an Fe center, which may catalyze the rearrangement to formate and H₂O, and to the fact that authentic samples of the hydroperoxide contain a higher concentration of water.

It is interesting to note that, according to gas and solution phase rate coefficients reported in the literature,^{12,18,19} 250 K is a far too low of a temperature for other reactions of CH₂OH and HOO radicals to play a role, except for addition to O₂. However, reactions with O₂ would merely constitute additional intermediate steps without altering the overall path presented in Scheme 1. For example, CH₂OH radical is known to add to O₂ at an essentially diffusion controlled rate to yield O₂CH₂–OH.¹⁸ Because the hydroxymethylperoxy radical reacts efficiently with HOO to give HO₂CH₂OH + O₂, intermediate steps involving O₂ would not alter the overall mechanism.¹²

The concurrent formation of formaldehyde indicates that HOO and CH₂OH not only combine to yield HO₂CH₂OH but also undergo H atom transfer to produce CH₂=O and H₂O₂. As shown in our previous paper,² CH₂=O reacts selectively with H₂O₂ in the presence of H₂O, CH₃OH, or lattice OH groups, and reaction with other formaldehyde molecules (Tishchenko and Cannizzaro reactions) is even less competitive. Because consumption of CH₂=O by addition to H₂O₂ to yield HO₂CH₂OH lasts 2.6 s, yet no induction period is observed for the subsequent HO₂CH₂OH → HCO₂⁻···Fe + H₂O rearrangement, the H atom transfer of HOO and CH₂OH can only be a minor channel.

The closest similarity in terms of mechanism for CH₃OH photooxidation by O₂ in other media is LMCT-mediated photochemistry of organo Fe^{+III} complexes in homogeneous solution. Visible light excitation of the LMCT transition of an Fe^{+III} complex in liquid methanol results in one-electron oxidation of a CH₃OH ligand to CH₃O radical under concurrent reduction of the metal to Fe^{+II}.²⁰ Subsequent oxidation of the radical by another Fe^{+III} complex yields CH₂=O. The catalytic cycle is closed by reoxidation of Fe^{+II} to Fe^{+III} by O₂. Although the LMCT-induced one-electron oxidation of CH₃OH to methoxy radical bears close resemblance to the mechanism in the FeAlPO₄ sieve, the subsequent chemistry of the primary radicals is different in the two cases (oxidation by second Fe^{+III} to formaldehyde (solution mechanism) versus direct coupling of one-electron transfer products to yield hydroxymethylhydroperoxide (sieve)). Methanol photooxidation has also been reported on various metal oxide surfaces, mostly TiO₂, or TiO₂-supported transition metal oxides. Proposed mechanisms for these heterogeneous systems differ significantly from that observed here in the Fe aluminophosphate sieve in that CH₃OH adsorbs dissociatively on the metal oxide as CH₃O. Absorption of light by the metal oxide is proposed to generate a hole on a surface oxide (O^{·-} radical anion), which abstracts a H atom from CH₃O to yield CH₂=O.^{21–23}

V. Conclusions

This time-resolved FT-IR study of CH₃OH photooxidation by O₂ in an Fe aluminophosphate sieve has revealed HO₂CH₂–OH as the main two-electron transfer intermediate. The fast rise of the intermediate on the submillisecond time scale (at 250 K) strongly suggests that it is formed by direct coupling of HOO and CH₂OH radicals, the presumed one-electron-transfer products of CH₃OH and O₂ interaction with the excited framework Fe center. It implies that the photogenerated Fe^{+II}–O^{·-} moiety