Mechanistic Study of $CH_3OH + O_2$ Photoredox Reaction in a $FeAlPO_4$ Sieve by Time-Resolved FT-IR Spectroscopy†

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The mechanism of the ligand-to-metal charge transfer (LMCT) induced reaction of methanol and O_2 at the gas−micropore interface of a $FeAlPO_4$-5 sieve has been studied by time-resolved FT-IR spectroscopy. Measurements using the rapid-scan method revealed that the final products, $HCO_2^-\cdots Fe$ and H_2O, emerge with a rise time of 4 s (250 K) by decomposition of the two-electron-transfer intermediate, HO_2CH_2OH. Intermediacy of hydroxymethylhydroperoxide was established by direct detection by step-scan FT-IR spectroscopy on the 500 microsecond time scale and by monitoring of its photodissociation products $HCO_2H + H_2O$ on the millisecond and second time scale. Formaldehyde was observed as minor two-electron oxidation product. The fast rise of the HO_2CH_2OH intermediate strongly suggests that it is formed by direct coupling of HOO and CH_2OH radicals. This constitutes the most conclusive evidence yet for the formation of a hydroperoxy radical and hydroxymethyl radical as the primary one-electron-transfer products of the reaction of CH_3OH and O_2 at LMCT-excited framework Fe centers.

I. Introduction

Substantial progress in the understanding of the multistep processes following interaction of donor and acceptor molecules with excited framework metals of molecular sieves is expected from in situ time-resolved monitoring of the chemistry. To obtain insight into the detailed mechanism of a prototypical redox reaction in a microporous material, we have employed rapid-scan and step-scan FT-IR spectroscopy to follow CH_3OH oxidation and O_2 reduction in a ligand-to-metal charge transfer (LMCT) excited Fe aluminophosphate sieve. A recent study in our laboratory of the 355 nm induced reaction of CH_3OH and O_2 gas adsorbed on $FeAlPO_4$-5 by static FT-IR spectroscopy gave formate ($HCO_2^-\cdots Fe$) and water as four-electron-transfer products.[1] Methyl formate emerged on a much longer time scale-upon condensation of HCO_2H with excess CH_3OH. Monitoring of the reaction on the millisecond and second time scale is expected to reveal the rise of these products and, possibly, the formation of two-electron-transfer intermediates such as formaldehyde and hydrogen peroxide proposed earlier.[1] No $CH_2{=}O$ was observed by static FT-IR spectroscopy despite its intense infrared bands, even when conducting the photochemistry at −100 °C. Our study of the adducts of the aldehyde with various species present upon methanol + O_2 reaction (H_2O, H_2O_2, CH_3OH, and lattice OH groups), reported in the preceding paper,[2] indicates that only hydroxymethylhydroperoxide, the addition product of $CH_2{=}O$ and H_2O_2, is sufficiently labile in the dark and under irradiation for playing a possible role as a two-electron-transfer intermediate. The molecule was found to dissociate in a FAPO-5 sieve in the dark or upon 355 nm excitation to HCO_2H ($HCO_2^-\cdots Fe$) and H_2O.[2]

In this paper, we report time-resolved FT-IR measurements on the microsecond to second time scale in order to elucidate the mechanism of the methanol + O_2 photoredox chemistry in the LMCT-excited $FeAlPO_4$-5 sieve.

II. Experimental Section

Self-supporting $FeAlPO_4$-5 wafers (AFI structure, abbreviated FAPO-5) were prepared and mounted in a miniature infrared vacuum cell as described in the preceding paper.[2] The infrared cell was mounted inside an Oxford model DN1714 cryostat. After dehydration at 473 K overnight under high vacuum, the temperature of the sieve was lowered for loading with 5 Torr of methanol and 700 Torr of O_2 (or N_2). Time-resolved photolysis experiments were conducted at 250 K unless noted otherwise.

Rapid scan FT-IR measurements[3,4] were conducted with a Bruker model IFS88 spectrometer. A highly sensitive HgCdTe photon detector Kolmar model KMPV8-1-J2 with an 8 micron band gap was used ($D^* = 1 \times 10^{11}$ cm Hz$^{1/2}$ W^{-1}). To maximize the sensitivity for spectroscopy in the fingerprint region, folding limits were chosen at 2106 and 1054 cm^{-1} requiring an infrared filter for blocking off probe light outside this range (OCLI model W07100-11X). Reaction was initiated by 355 nm nanosecond pulses (third harmonic) of either a Nd:YAG laser Coherent model Infinity or Quanta Ray model DCR2A (with GCR-3 upgrade). A small quartz prism (1 cm edge-to-edge) was used to align the photolysis beam collinearly with the infrared probe beam. To prevent photolysis light entering the detector or interferometer compartment, the ports to these compartments were closed off by 2 in. germanium plates with dielectric coatings that maximized infrared transmission ($T = 95\%$, International Scientific).

Experiments were conducted on the millisecond and second time scale. One method for obtaining millisecond spectra

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consisted of recording an interferogram of 109 ms duration (double-sided/forward−backward) at a fixed delay of 12 ms after the 355 nm laser pulse. The mirror velocity was 160 kHz, and the spectral resolution was 4 cm^{-1}. Start of the interferogram acquisition following a laser pulse was triggered by an optical pulse diverted from the photolysis laser beam (Si photodiode EG&G model SGD-444). To ensure that the time delay between the laser pulse and the start of interferogram acquisition was the same after each pulse (12.0 ± 0.2 ms), the Nd:YAG laser was triggered by a TTL pulse from the FT-IR instrument coincident with the forward turn of the moving mirror. The TTL pulse was sent through a home-built rate divider before entering the laser in order to suppress all pulses during a 2.56 s period needed for the transient species to decay (section III). A second interferogram was recorded and stored during the last forward−backward motion of the mirror just before the next photolysis pulse. A total of 200 such sets of interferogram pairs (hence, single beam spectra) resulting from 200 laser pulses were stored and constitute an "experiment". Final 100 ms spectra were obtained by ratioing the single beam spectrum just after the *n*th pulse against the single beam spectrum just before that pulse. The 200 ratioed spectra from the 200 pulses were then averaged, furnishing the 100 ms absorbance spectrum of that experiment. A total of 40 such experiments were conducted and averaged in order to improve the S/N ratio. Calculations were carried out with a MACRO program executed within the Bruker OPUS software. A second method of measuring millisecond spectra consisted of recording a (single-sided/forward only) interferogram of 25 ms duration at a fixed delay of 11 ms after the 355 nm pulse. Separation of laser pulses was 73 ms. A total of 200 such interferograms resulting from 200 laser pulses were stored separately. Final 25 ms spectrum of the experiment was obtained by ratioing the single beam spectrum of the *n*th pulse against the single beam spectrum of pulse $n - 1$, and averaging all 200 absorbance spectra. Typically, 10 such experiments were conducted and averaged to improve the sensitivity.

Slow runs on the time scale of seconds were conducted in two ways. The first method consisted of the recording of 99 interferograms following a single Nd:YAG laser pulse (double-sided/forward−backward at 160 kHz and 4 cm^{-1} resolution). Again, the laser was triggered by the forward motion of the interferometer mirror, using a rate divider to suppress TTL pulses from the FT-IR instrument for a period of 12.8 s between laser pulses. A total of 10 consecutive interferograms were automatically averaged, furnishing interferogram time slices (stored in "buffers") at 1.28 s resolution. To simplify the data analysis, buffers Nos. 6−9 were averaged to yield a single time slice of 5.1 s duration. Hence, the data stored after each photolysis pulse consisted of seven averaged interferograms (resulting in seven single beam spectra) taken at 0.6, 1.9, 3.2, 4.5, 5.8, 9.0, and 12.2 s after the laser pulse (midpoints). A total of 50 such sets of seven single beam spectra generated by 50 laser pulses were stored as the result of one experiment. Final time-resolved spectra for a given time delay were obtained by ratioing each of the 50 corresponding stored single beam spectra (one of the seven averages after each pulse) against the single beam spectrum taken just before the pulse. These 50 ratioed spectra were then average to yield the absorbance time slice for a given delay. The results of 5−10 such experiments were further averaged for S/N improvement.

In our second approach for obtaining rapid scan spectra on the time scale of seconds, we employed substantially longer photolysis light exposure while using the same method of interferogram recording just described. The sample was again excited 50 times at intervals of 12.8 s, but each exposure consisted of 10 laser pulses over a period of 1.1 s. This was accomplished by passing the 355 nm Nd:YAG beam (train of 10 Hz pulses) through a mechanical shutter (UniBlitz driver model D122 with a head (Vincent Assoc.) featuring a 13 mm diameter aperture) of 1.1 s duration. Opening of the shutter was initiated by a TTL pulse of the FT-IR instrument synchronous with a forward turn of the moving mirror. Data were evaluated as described for the first method. The first buffer contained the average of the spectra recorded *during* 1.1 s irradiation, and subsequent spectra correspond to delays of 0.8, 2.1, 3.4, 4.7, 7.9, and 11.1 s after completion of photolysis light exposure.

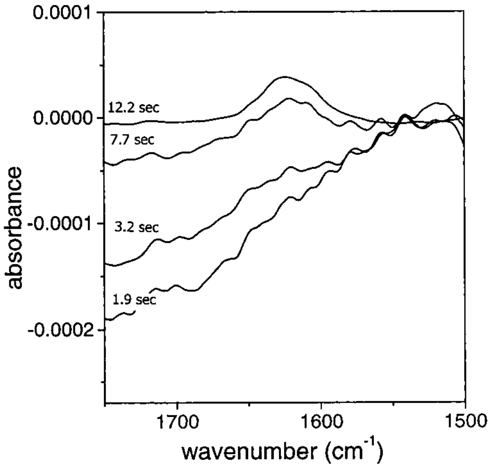


Figure 1. Rapid-scan FT-IR spectra on the second time scale of $CH_3OH + O_2$ photoreaction induced by single 355 nm pulses in a FAPO-5 sieve at 250 K.

Experiments in the step-scan mode at 5 μs resolution were conducted with the same spectrometer, using methods described in detail in previous reports.[5−7] The same HgCdTe infrared detector was used as in the rapid-scan runs. Measurements focused on the spectral region 1550−1350 cm^{-1} using folding limits 1606 and 1339 cm^{-1} and a band-pass filter (University of Reading Infrared Multilayer Laboratory model 21K), installed in front of the infrared detector. Spectral resolution was 4 cm^{-1}, resulting in step-scan runs involving 135 mirror positions. At each mirror position, five laser-induced decays were recorded and averaged. Photolysis pulses were separated by 100 ms.

Methanol (EM Science, 99.8%), methanol-D_4 (Aldrich, 99%D), and methanol-^{13}C (Aldrich, 99%^{13}C) were degassed by freeze−pump−thaw cycles before use. Oxygen and nitrogen gas (Air Products, 99.997%) were used as received. Hydroxymethyl-hydroperoxide was synthesized inside FAPO-5 by reaction of H_2O_2 loaded into the sieve with adsorbed $CH_2{=}O$ gas according to the method described in the preceding paper[2].

III. Results

To find out about the reaction steps immediately preceding formation of the final products, rapid scan runs were conducted on a time scale of seconds. Experiments using single 355 nm photolysis pulses followed by recording of interferograms over a period of 12.8 s revealed the growth of $HCO_2^- \cdots Fe$ at 1625 cm^{-1}, which is complete within 10 s at 250 K. The band, which is assigned to (symmetric) formate based on the characteristic 10 cm^{-1} isotope shift of $HC^{18}O^{16}O^-$, overlaps with H_2O coproduct.[1] Figure 1 shows rapid-scan spectra recorded 1.9, 3.2, 7.7, and 12.2 s after the pulse. The result of five 50-shot experiments of the $CH_3OH + N_2$ system was subtracted from the spectra of $CH_3OH + O_2$ runs to cancel out methanol

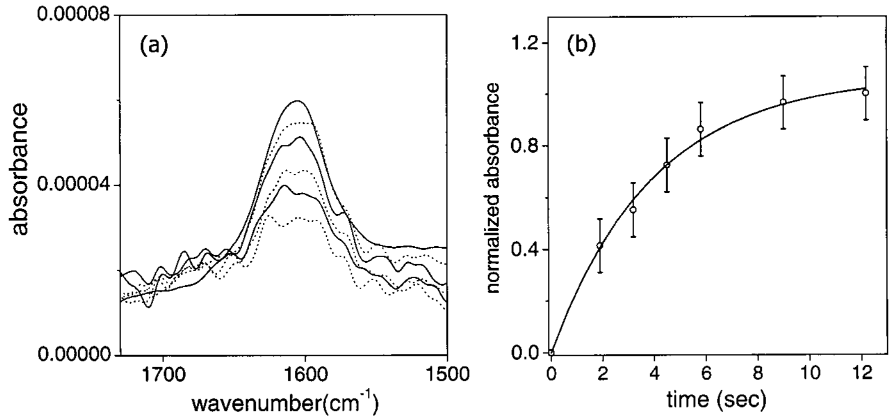


Figure 2. (a) Rapid-scan FT-IR spectra of single pulse-induced $CD_3OD + O_2$ photoreaction in a FAPO-5 sieve at 250 K recorded at 1.9, 3.2, 4.5, 5.8, 9.0, and 12.2 s after the 355 nm pulse. Alternate traces are dashed for clarity. (b) Single-exponential fit of (peak) absorbance growth gives a rise constant of $0.25 + 0.02\ s^{-1}$.

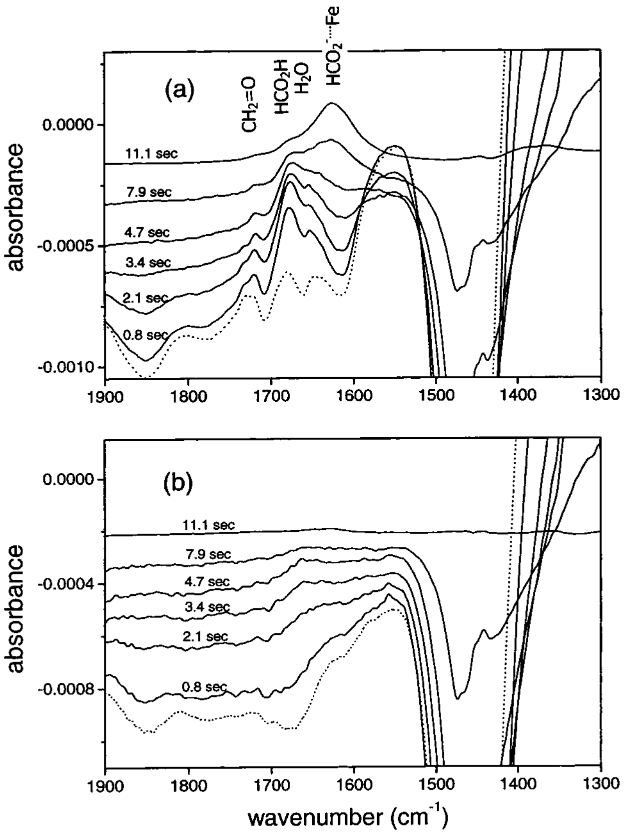


Figure 3. (a) Rapid-scan FT-IR spectra of 355 nm induced $CH_3OH + O_2$ reaction in a FAPO-5 sieve at 250 K. Spectra were recorded on the second time scale following excitation for 1.1 s by a sequence of 355 nm pulses at 10 Hz. Dotted trace is spectrum recorded during laser irradiation. (b) Result of identical experiment for the $CH_3OH + N_2$ system.

desorption effects (see below). More accurate data were obtained from a $CD_3OD + O_2$ study as desorption-induced changes of methanol are outside the 2000−1300 cm^{-1} spectral range for this isotope and are presented in Figure 2a. A single-exponential fit gives a rise of $DCO_2^{-}\cdots Fe$ of $0.25 + 0.02\ s^{-1}$ (Figure 2b).

A 10-fold improvement of the S/N ratio was accomplished by using a train of 10 photolysis pulses instead of a single pulse. Figure 3a shows the transient absorbance spectrum of the parent $CH_3OH + O_2$ reaction. The dotted trace was recorded during 1.1 s photolysis, the subsequent curves at delays of 0.8, 2.1, 3.4, 4.7, 7.9, and 11.1 s after completion of the photolysis period.

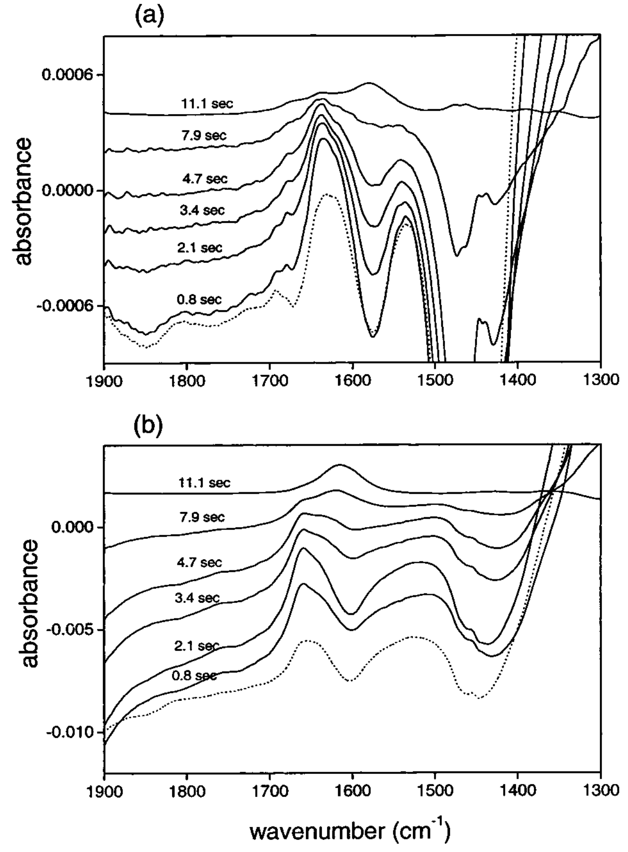


Figure 4. Rapid-scan FT-IR experiment on the second time scale as described in Figure 3 for (a) $^{13}CH_3OH + O_2$ and (b) $CD_3OD + O_2$.

As in the previous studies, the sieve temperature was held at 250 K. The strong bleach in the 1500−1350 cm^{-1} region is due to consumption of methanol by reaction, as well as by desorption caused by a laser-induced temperature rise of a few degrees. The spectral effects of methanol desorption due to the laser pulse can be seen when conducting experiments with N_2 instead of O_2, shown in Figure 3b. Readsorption is complete within about 10 s. The transient absorbance spectrum recorded during photolysis (dotted curve of Figure 3a) reveals the $CH_2{=}O$ band centered at 1726 cm^{-1}. Figure 4a shows the corresponding $^{13}CH_2{=}O$ absorption at 1687 cm^{-1} in similar runs with $^{13}CH_3OH + O_2$. The formaldehyde band is sufficiently separated from the nearest absorption to allow us to estimate the lifetime

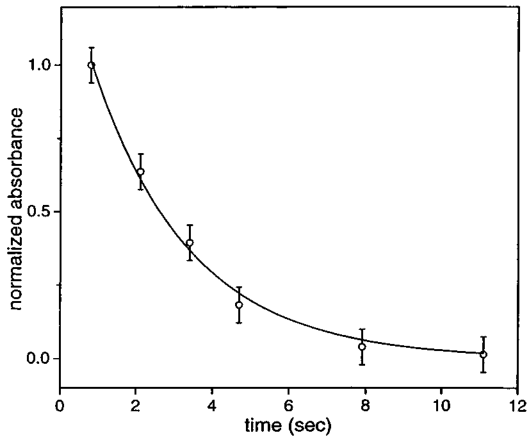


Figure 5. Single-exponential fit of absorbance decay at 1726 cm^{-1} (Figure 3) yields decay constant of $0.38 \pm 0.03\ s^{-1}$.

of the intermediate. As shown in Figure 5, a single-exponential fit of the integrated absorbance decay gives a $1/e$ time of 2.6 ± 0.2 s.

In addition to observing formaldehyde (1726 cm^{-1}) and growth of formate at 1625 cm^{-1}, spectra of Figure 3a reveal strong transient absorptions not seen in the single pulse experiments (Figure 2a). The main band at 1679 cm^{-1} is assigned to HCO_2H, the shoulder around 1650 cm^{-1} is assigned to the H_2O coproduct. These assignments are confirmed by observation of transient $H^{13}CO_2H$ at 1638 cm^{-1} (coinciding with H_2O) in rapid-scan runs of $^{13}CH_3OH + O_2$ (Figure 4a), and DCO_2H at 1660 cm^{-1} in experiments with CD_3OD (Figure 4b).[1,2,9,10] $H^{13}CO_2H$ and DCO_2H convert to $H^{13}CO_2^{-}\cdots Fe$ (1578 cm^{-1}) and $DCO_2^{-}\cdots Fe$ (1615 cm^{-1}), respectively, within 10 s. We conclude that formic acid emerges as an intermediate in rapid-scan experiments but only when irradiating with multiple laser pulses in rapid succession (100 ms between pulses). This points to secondary photolysis of a reaction intermediate as the source of HCO_2H.

According to our recent study of addition products of formaldehyde with various molecules that are present in the $CH_3OH + O_2$ reaction mixture, only hydroxymethylhydroperoxide is photolabile upon irradiation at 355 nm in a FAPO-5 sieve.[2] To determine the photoproducts, time-resolved experiments of HO_2CH_2OH photodissociation in a FAPO-5 sieve were performed on the millisecond time scale. Because of the thermal instability of the hydroperoxide (half-life 20 min at 296 K)[2], FT-IR runs were conducted immediately following room-temperature adsorption of $CH_2{=}O$ gas onto the H_2O_2-loaded sieve. Rapid-scan experiments consisted of acquisition of interferograms of 25 ms duration according to the procedure described in section II. A 200 laser shot experiment lasted 15 s, which guaranteed negligible thermal decomposition of the hydroxymethylhydroperoxide during the rapid-scan experiment. Absorbance spectra were obtained by ratioing and then averaging consecutive single beam spectra.

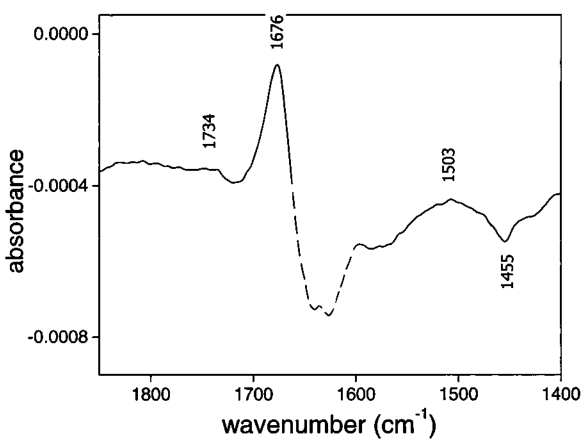


Figure 6. Rapid-scan FT-IR spectroscopy of 355 nm induced HO_2-CH_2OH photodissociation in a FAPO-5 sieve at 25 ms resolution (298 K). Dashed part of the spectrum indicates laser-induced thermal effect on residual water.

The resulting spectrum, displayed in Figure 6, shows the photoinduced depletion of HO_2CH_2OH at 1455 cm^{-1}. The predominant product band is at 1676 cm^{-1} and originates from HCO_2H. The depletion in the 1650−1620 cm^{-1} range (dashed line) is due to a laser-induced thermal effect on the large absorption of residual H_2O (hydrogen peroxide is loaded into the sieve as a 30% aqueous solution). For the same reason, any formation of H_2O upon HO_2CH_2OH photodissociation would not be detectable. Very weak absorptions at 1734 and 1503 cm^{-1} signal the formation of a small amount of $CH_2{=}O$. Hence, two photodecomposition channels are operative, namely, the major channel

$$HO_2CH_2OH \xrightarrow{h\nu} HCO_2H + H_2O \tag{1}$$

and the minor path

$$HO_2CH_2OH \xrightarrow{h\nu} CH_2{=}O + H_2O_2 \tag{2}$$

(Note that the formaldehyde coproduct, H_2O_2, does not possess an infrared absorption in the 2000−1300 cm^{-1} region).[11] It is interesting to add that both channels are also observed upon photodissociation of the molecule in homogeneous solution.[12] We conclude that the formic acid product observed in Figures 3 and 4 originates most probably from secondary photolysis of hydroxymethylhydroperoxide intermediate. Because no HCO_2H is detected upon single pulse-induced $CH_3OH + O_2$ photolysis and because formaldehyde is only a minor photodissociation product of HO_2CH_2OH, the $CH_2{=}O$ growth observed in the rapid-scan experiments is exclusively due to single photon reaction of CH_3OH and O_2.

To obtain direct evidence for the intermediacy of HO_2CH_2OH, we have measured time-resolved FT-IR spectra on the microsecond time scale by employing the step-scan method. Of the three absorptions observed for an authentic hydroxymethylhydroperoxide sample in the FAPO-5 sieve (1456, 2884, and 2948 cm^{-1})[2], the CH stretching modes are in a region where the sieve scatters strongly, resulting in a noise level that is too high for step-scan measurements. Therefore, we have concentrated the measurements on the absorption in the fingerprint region. Figure 7 shows the 500 μs time slices of step-scan runs of $CH_3OH + O_2$ (trace a) and $CH_3OH + N_2$ (trace b). Aside from the methanol desorption effect around 1475 cm^{-1}, there is positive growth at 1450 cm^{-1}, which we attribute to HO_2-CH_2OH. The product band is most clearly evident from the O_2-N_2 difference spectrum shown in the insert. Note that the observed absorbance growth at 1450 cm^{-1} due to $CH_3OH + O_2$ photoreaction is diminished by simultaneous depletion upon photodissociation of HO_2CH_2OH that remains from the preceding laser pulse.

IV. Discussion

A key result of the rapid-scan experiments is that the rise of the final product $HCO_2^{-}\cdots Fe$ follows a single-exponential law

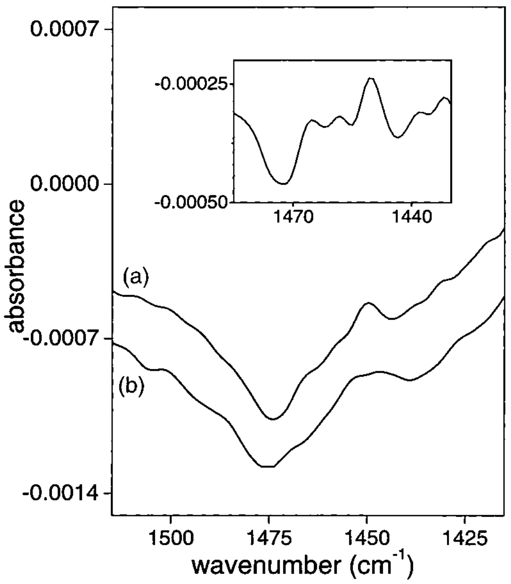
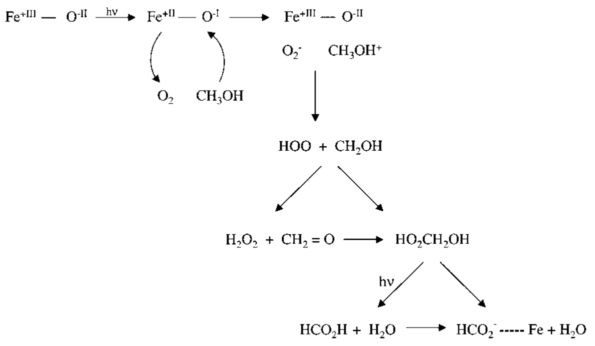


Figure 7. (a) Step-scan FT-IR spectrum of $CH_3OH + O_2$ photoreaction in a FAPO-5 sieve at 250 K (co-addition of 100 5 μs time slices). (b) Identical experiment for $CH_3OH + N_2$ system. The insert shows the difference of traces a and b.

SCHEME 1



and does not exhibit a distinct induction period. This implies that HO_2CH_2OH, 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 $CH_3OH + O_2$ photolysis. Hence, the HO_2CH_2OH intermediate is most probably formed by direct coupling of HOO and CH_2OH radicals rather than reaction of $CH_2{=}O + H_2O_2$, which takes 2.6 s (250 K). Scheme 1 describes the proposed mechanism. Absorption of a photon by the $Fe^{+III}{-}O^{-II} \rightarrow Fe^{+II}{-}O^{-I}$ LMCT transition results in a transiently reduced Fe center and a hole on a framework oxygen. The initial electron-transfer steps are reduction of O_2 by Fe^{+II} to O_2^- and concurrent oxidation of CH_3OH by the electron-deficient framework O to the alcohol radical cation. The highly acidic CH_3OH^+ is expected to undergo proton transfer to superoxide to form HOO and CH_3O radicals. The latter is unstable relative to CH_2OH, and isomerization of CH_3O to CH_2OH is known to proceed extremely fast.[13-15] In the gas or solution phase, the coupling of HOO and CH_2OH radicals is close to diffusion controlled.[16,17] The resulting two-electron-transfer product, HO_2CH_2OH, rearranges spontaneously to $HCO_2^-\cdots Fe$ and H_2O, the products observed previously by static FT-IR spectroscopy[1]. Hence, the overall chemistry is a single photon-induced four-electron-transfer process with HO_2CH_2OH as the main closed-shell intermediate. Thermal disproportionation of hydroxymethylhydroperoxide to formate and H_2O in the case of the photochemical $CH_3OH + O_2$ system is much faster than for authentic samples of HO_2CH_2OH or HO_2CD_2OH loaded into the sieve, or synthesized in situ by co-loading of H_2O_2 and $CH_2{=}O$.[2] We attribute this to the fact that photochemically produced HO_2CH_2OH is generated at an Fe center, which may catalyze the rearrangement to formate and H_2O, 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 CH_2OH and HOO radicals to play a role, except for addition to O_2. However, reactions with O_2 would merely constitute additional intermediate steps without altering the overall path presented in Scheme 1. For example, CH_2OH radical is known to add to O_2 at an essentially diffusion controlled rate to yield O_2CH_2OH.[18] Because the hydroxymethylperoxy radical reacts efficiently with HOO to give $HO_2CH_2OH + O_2$, intermediate steps involving O_2 would not alter the overall mechanism.[12]

The concurrent formation of formaldehyde indicates that HOO and CH_2OH not only combine to yield HO_2CH_2OH but also undergo H atom transfer to produce $CH_2{=}O$ and H_2O_2. As shown in our previous paper,[2] $CH_2{=}O$ reacts selectively with H_2O_2 in the presence of H_2O, CH_3OH, or lattice OH groups, and reaction with other formaldehyde molecules (Tishchenko and Cannizzaro reactions) is even less competitive. Because consumption of $CH_2{=}O$ by addition to H_2O_2 to yield HO_2CH_2OH lasts 2.6 s, yet no induction period is observed for the subsequent $HO_2CH_2OH \rightarrow HCO_2^-\cdots Fe + H_2O$ rearrangement, the H atom transfer of HOO and CH_2OH can only be a minor channel.

The closest similarity in terms of mechanism for CH_3OH photooxidation by O_2 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 CH_3OH ligand to CH_3O radical under concurrent reduction of the metal to Fe^{+II}.[20] Subsequent oxidation of the radical by another Fe^{+III} complex yields $CH_2{=}O$. The catalytic cycle is closed by reoxidation of Fe^{+II} to Fe^{+III} by O_2. Although the LMCT-induced one-electron oxidation of CH_3OH to methoxy radical bears close resemblance to the mechanism in the $FeAlPO_4$ 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 TiO_2, or TiO_2-supported transition metal oxides. Proposed mechanisms for these heterogeneous systems differ significantly from that observed here in the Fe aluminophosphate sieve in that CH_3OH adsorbs dissociatively on the metal oxide as CH_3O. Absorption of light by the metal oxide is proposed to generate a hole on a surface oxide (O^{-I} radical anion), which abstracts a H atom from CH_3O to yield $CH_2{=}O$.[21-23]

V. Conclusions

This time-resolved FT-IR study of CH_3OH photooxidation by O_2 in an Fe aluminophosphate sieve has revealed HO_2CH_2OH 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 CH_2OH radicals, the presumed one-electron-transfer products of CH_3OH and O_2 interaction with the excited framework Fe center. It implies that the photogenerated $Fe^{+II}{-}O^{-I}$ moiety reacts with the donor, CH_3OH, and acceptor, O_2, on a time scale of microseconds or faster. H atom transfer of HOO and CH_2OH radicals to yield $CH_2{=}O$ and H_2O_2 is only a minor reaction path.

Time-resolved rapid-scan and step-scan FT-IR methods afford a new level of mechanistic insight into photoreactions inside molecular sieves. Elucidation of elementary reaction steps from primary intermediates to stable products is essential for identifying transition metal molecular sieves for desired photochemical transformations.

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