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Chemical Reactivity of Formaldehyde in a $FeAlPO_4$ Sieve[†]

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Formaldehyde gas loaded into a framework Fe aluminophosphate sieve ($FeAlPO_4$-5) at 250 K was found to react with adsorbed H_2O, CH_3OH, H_2O_2, or lattice OH groups to yield the corresponding addition products, namely, $CH_2(OH)_2$, CH_3OCH_2OH, HO_2CH_2OH, or $POCH_2OH$, respectively. Reactions were monitored in situ by static FT-IR spectroscopy, and assignments are based on experiments with $CD_2{=}O$ and CD_3OD. Most efficient was the reaction with H_2O_2, as indicated by the fact that HO_2CH_2OH was formed at the exclusion of $CH_2(OH)_2$ and $POCH_2OH$ when adsorbing formaldehyde onto a sieve loaded with H_2O_2 and H_2O. Methoxymethanol, methanediol, and $POCH_2OH$ were stable at 250 K but dissociated above 0 °C under release of formaldehyde. Hydromethyl hydroperoxide disproportionates to formic acid and water. Under 355 nm irradiation in a $FeAlPO_4$ sieve, HO_2CH_2OH was found to undergo efficient photofragmentation.

I. Introduction

The constrained environment of microporous solids, combined with the robust nature of framework transition metals as chromophores and redox centers, offers opportunities for accomplishing demanding photosynthetic transformations. For small molecules, the gas−micropore interface is a particularly suitable reaction environment. The key to a successful search for transition metals and frameworks for a desired photochemical transformation is the knowledge of the redox properties of excited metal centers and a detailed mechanistic understanding of how reactants interact with the framework redox sites. We have recently employed in situ FT-IR spectroscopy to probe the reactivity of ligand-to-metal charge transfer (LMCT) excited Fe centers of $FeAlPO_4$-5 (abbreviated FAPO-5) molecular sieve.[1] The material consists of a one-dimensional system of 7.3 Å diameter channels.[2] O_2 was used as electron acceptor, and methanol was used as a donor. Formic acid (formate), H_2O, and methyl formate were observed as final products, the latter emerging from a slow ester condensation of HCO_2H and excess CH_3OH. Formaldehyde and H_2O_2 were proposed as two-electron-transfer intermediates. These species could not be detected even when conducting the photoreaction at −100 °C.

In our effort to experimentally establish the step-by-step mechanism of this prototypical photoredox reaction at framework Fe centers, we have investigated the fate of formaldehyde in such a reaction environment. The lack of observation of formaldehyde could, in principle, be due to efficient reaction with CH_3OH, framework OH groups, or coproducts H_2O_2 or H_2O. To find out about the formation of such adducts and their possible role in the $CH_3OH{+}O_2$ photoreaction, we report here an FT-IR study of formaldehyde interactions with various small molecules in FAPO-5 sieve. Knowledge of the spectra and stability of these adducts is a prerequisite for interpreting time-resolved FT-IR experiments of the $CH_3OH{+}O_2$ photoreaction.

II. Experimental Section

Synthesis and characterization of FAPO-5 materials used were described in detail in a previous report.[1] Self-supporting wafers of about 10 mg weight and 1 cm diameter were prepared with a KBr press and mounted in a miniature infrared vacuum cell equipped with CaF_2 windows. The cell was situated inside an Oxford Cryostat model DN1714, allowing us to vary the matrix temperature between 77 and 473 K with a programmable Oxford Controller model ITC-503. For each loading experiment, a pellet was prepared and dehydrated at 200 °C under high vacuum (2×10^{-6} Torr) using a turbomolecular pump (Varian model V-70). Gases were loaded into the molecular sieve through glass or stainless steel manifolds. Infrared spectra were recorded at 1 cm^{-1} resolution using a Bruker model IFS88 FT-IR spectrometer equipped with a HgCdTe photon detector model Kolmar KMPV8-1-J2. Photochemical behavior of products under 355 nm irradiation was studied using the third harmonic emission of a Coherent laser model Infinity (10 Hz, 50 mJ cm^{-2} $pulse^{-1}$).

Methanol (EM Science, 99.8%) and methanol-D_4 (Aldrich, 99% D) were degassed by freeze−pump−thaw cycles before use. Formaldehyde gas was obtained by depolymerization of paraformaldehyde (Aldrich, 95%) or deutero paraformaldehyde (Cambridge Isotope Laboratories, 99% D) and purified according to literature procedure.[3] Hydrogen peroxide was loaded into the molecular sieve by putting one drop of H_2O_2/H_2O solution (30%, Sigma) onto the pellet mounted inside the infrared vacuum cell. Formaldehyde gas was added after evacuating the pellet for five minutes at room temperature.

III. Results and Discussion

Methanol + Formaldehyde. Loading of 5 Torr of CH_3OH gas into a FAPO-5 sieve at 250 K gave infrared bands at 1347 (shoulder), 1436, 1472, 2843, 2956, 3250, and 3619 cm^{-1}. Subsequent exposure of the sieve to 2 Torr of $CH_2{=}O$ resulted in instantaneous depletion of methanol under concurrent formation of a product whose infrared spectrum is shown in Figure

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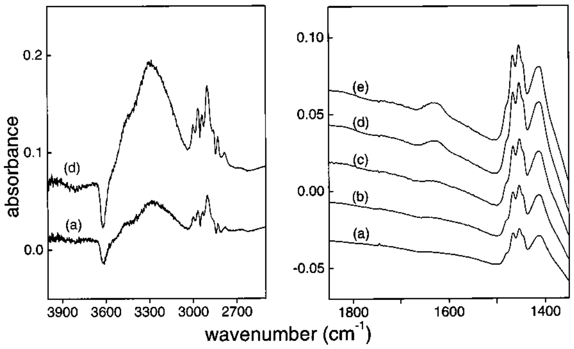

Figure 1. Infrared difference spectra before and after admission of 2 Torr of $CH_2=O$ into FAPO-5 loaded with CH_3OH at 250 K. (a) 2 min, (b) 8 min, (c) 18 min, (d) 60 min, and (e) 90 min after exposure to $CH_2=O$ gas. The weak band at 1628 cm^{-1} emerging after 60 min is due to $HCO_2^{-}\cdots Fe$.

TABLE 1: Absorption Frequencies of Methanol + Formaldehyde Product in a FAPO-5 Sieve (in cm^{-1})

reaction product			
CH_3OH + $CH_2=O$ → CH_3OCH_2OH	CH_3OH + $CD_2=O$ → CH_3OCD_2OH	$CD_3OD(H)$ + $CH_2=O$ → $CD_3OCH_2OD(H)$	assignment[a]
1412		1415	$\gamma_w(CH_2)$
	1443 (sh)		
1452	1454		$\delta_a(CH_3)$
1466	1467		$\delta_a(CH_3)$
1480		1481	$\delta(CH_2)$
		2069	$\nu_s(CD_3)$
	2094		$\nu_s(CD_2)$
	2198		$\nu_a(CD_2)$
		2220	$\nu_a(CD_3)$
	2245		$\nu_a(CD_2)$
		2450 (broad)	ν (OD)
2782		2786	ν_s (CH_2)
2829	2833		ν_s (CH_3)
2901		2901	ν_a (CH_2)
	2911		
2938	2938		ν_a (CH_3)
2966		2966	ν_a (CH_2)
3000	3002		ν_a (CH_3)
3280 (broad)	3280 (broad)	3280 (broad)	$\nu(OH)$

[a] Same assignment for more than one product band implies site or Fermi resonance effects.

1, trace a. All bands observed are listed in Table 1, first column. Although growth continues over a period of about 90 min (Figure 1b−e), the product spectrum is already well developed immediately after $CH_2=O$ loading. Hence, the reaction of formaldehyde with methanol is fast compared with the time scale on which the static FT-IR spectra are taken (2 min). The implication is that the reaction has a very low activation barrier. The only product we can conceive of that involves a low activation energy and has no C=O group (no product absorption around 1700 cm^{-1}) is methoxymethanol, CH_3OCH_2OH[4] (the weak, broad band at 1630 cm^{-1} exhibits an induction period and is due to formate, $HCO_2^{-}\cdots Fe$ [1]. Its origin will be discussed below). The infrared frequencies shown in column 1 of Table 1 agree with those reported for CH_3OCH_2OH in the gas phase[5] or isolated in solid Ar.[6] Assignments presented in the last column of Table 1 are based on quantum chemical work reported by Wrobel et al.[6]

The identification of the product as methoxymethanol was confirmed by D isotope labeling experiments. As in the case with the parent isotopes, initial reaction of $CD_2=O$ adsorbed into the FAPO-5 sieve loaded with CH_3OH was too fast for the detection of formaldehyde by static FT-IR spectroscopy. The resulting product spectrum is shown in Table 1, column 2. Only half as many bands are observed in the CH bending region as in the case of CH_3OCH_2OH, indicating that the 1454 and 1467 cm^{-1} peaks are due to modes of the CH_3 group. The three absorptions in the CD stretching region at 2094, 2198, and 2245 cm^{-1} are attributed to the CD_2 group (or Fermi resonance with overtone), and the 2833, 2911, 2938, and 3002 cm^{-1} bands are attributed to stretching modes and Fermi resonances involving overtones of the CH_3 group of CH_3OCD_2OH. These assignments, and identification of the product as methoxymethanol, are further corroborated by the spectrum observed upon co-loading of CD_3OD and $CH_2=O$ given in column 3 of Table 1. Upon adsorption of the alcohol (before loading of $CH_2=O$), the spectrum of CD_3OD shows bands at 2076, 2137, 2244, 2500 (broad), and 2664 cm^{-1}. The latter two absorptions are assigned to $\nu(OD)$ of methanol hydrogen bonded to the micropore wall and to free $\nu(OD)$ of OD groups, respectively. Weaker $\nu(OH)$ absorptions at 3250 and 3610 cm^{-1} indicate formation of CD_3-OH by partial exchange of the OD groups with residual H_2O in the sieve or with lattice OH groups. Upon adsorption of $CH_2=O$, bands appear in the CH bending region at 1415 and 1481 cm^{-1} and at 2786, 2901, and 2966 cm^{-1} in the $\nu(CH)$ region. Because these are observed in the CH_3OCH_2OH spectrum, but not in the CH_3OCD_2OH spectrum, they are attributed to the CH_2 group. Similarly, the 2069 and 2220 cm^{-1} peaks in the CD stretching region are missing in the CH_3OH + $CD_2=O$ product and, hence, are assigned to the CD_3 group. We conclude that, in a FAPO-5 sieve, formaldehyde adds to methanol to yield methoxymethanol, the hemiacetal being formed in a matter of minutes or faster at 250 K.

Warm up of the sieve to room temperature upon formation of methoxymethanol at 250 K resulted mostly in desorption of the product. Above 0 °C, growth of absorptions in the C=O stretching region indicated very slow generation of methyl formate: 1717 cm^{-1} (HCO_2CH_3) in the case of CH_3OCH_2OH; 1708 cm^{-1} (HCO_2CD_3) for CD_3OCH_2OH; and 1685 cm^{-1} (DCO_2CH_3) in the case of CH_3OCD_2OH. This process is attributed to dissociation of methoxymethanol to methanol and formaldehyde, followed by Tishchenko dimerization of the aldehyde or Cannizzaro reaction with residual H_2O (as indicated by very slow formation of HCO_2^{-}) followed by ester condensation with methanol to yield methylformate[1].

Loading of Formaldehyde in the Presence of Water. Recording of an infrared spectrum immediately following adsorption of 2 Torr of $CH_2=O$ at 250 K into a dehydrated pellet gave the familiar spectrum of formaldehyde in FAPO-5 with peaks at 1503, 1732, 2824, 2898, and 2990 cm^{-1} reported earlier,[1] as well as residual gas-phase absorptions with Q branches at 1503 and 1745 cm^{-1}.[7] The spectrum is displayed in Figure 2, trace a. As can be seen from trace b, peaks appear within minutes at 1400, 1422, 1472, and 1484 cm^{-1} and also at 2795, 2913, 2978, and 3200 cm^{-1}, with little further growth at later times. Concurrently, all $CH_2=O$ peaks decrease, and a small bleach is observed at 1650 cm^{-1} coincident with the bending mode of residual H_2O (upon heating of the pellet at 200 °C overnight, the residual absorbance of H_2O at 1650 cm^{-1} is typically 0.15). In addition, the OH stretch absorption of lattice P−OH groups[1] at 3674 cm^{-1} shows loss of intensity as well (Figure 2). This suggests that both P−OH groups and residual H_2O react with adsorbed formaldehyde. To distinguish the product spectra, a FAPO-5 pellet with a higher concentration of water was prepared by loading 2 Torr of H_2O gas into the sieve after dehydration at 200 °C. The additional increase of the H_2O bending mode intensity was 0.1 absorbance units. A

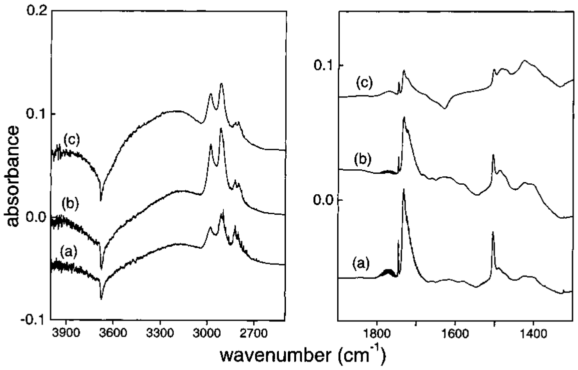

Figure 2. Infrared difference spectra recorded upon adsorption of 2 Torr of $CH_2{=}O$ on a FAPO-5 sieve at 250 K (a) immediately after loading and (b) 3 min later. Trace c shows the infrared difference spectrum recorded upon adsorption of 1.3 Torr $CH_2{=}O$ onto a FAPO-5 sieve loaded with 2 Torr H_2O after dehydration of the pellet.

TABLE 2: Absorption Frequencies of Adducts of Formaldehyde with H_2O and Lattice P−OH Groups in a FAPO-5 Sieve (in cm^{-1})

reaction product		
$CH_2{=}O$ loading	$CD_2{=}O$ loading	assignment
1400		$\gamma_w(CH_2)$, $POCH_2OH$
1425		$\gamma_w(CH_2)$, $CH_2(OH)_2$
1470		$\delta(CH_2)$, $POCH_2OH$
1483		$\delta\,(CH_2)$, $POCH_2OH$
	2105	$\nu_s(CD_2)$, $POCD_2OH$
	2138	$\nu_s(CD_2)$, $CD_2(OH)_2$
	2225 (sh)	$\nu_a(CD_2)$, $POCD_2OH$
	2254	$\nu_a(CD_2)$, $CD_2(OH)_2$
2796		$\nu_s(CH_2)$, $POCH_2OH$
2912		$\nu_a(CH_2)$, $POCH_2OH$
2980		$\nu_a(CH_2)$, $CH_2(OH)_2$
3200 (broad)	3200 (broad)	$\nu(OH)$, $CH_2(OH)_2$, $POCH_2OH$ $CD_2(OH)_2$, $POCD_2OH$

difference spectrum taken immediately after addition of 1 Torr $CH_2{=}O$ into this matrix, shown in Figure 2c, exhibits the same product bands as those observed in trace b. Depletion of H_2O around 1650 cm^{-1} and of ν(OH) of P−OH groups at 3674 cm^{-1} again indicates that both H_2O and lattice hydroxyl groups interact with formaldehyde. Product bands at 1425 and 2980 cm^{-1} are more intense in the spectrum in Figure 2 part c than those in part b, however. Hence, they are assigned to $CH_2(OH)_2$, the expected reaction product of H_2O and $CH_2{=}O$:

$$CH_2{=}O + H_2O \rightarrow CH_2(OH)_2 \qquad (1)$$

Indeed, the two bands agree well with the infrared spectrum of methanediol isolated in solid Ar.[8] All other product absorptions (except 1676 cm^{-1}, see below) are attributed to the addition product of $CH_2{=}O$ and lattice OH groups

$$(O-)_3P-OH + CH_2{=}O \rightarrow (O-)_3P-OCH_2OH \qquad (2)$$

Bands assigned to $P-OCH_2OH$ agree well with literature values for CH_2 stretching and bending modes of $P-O-CH_2$ moieties.[9] Frequencies and assignments of the reaction products of $CH_2{=}O$ with H_2O and P−OH are summarized in column 1 of Table 2. It is important to note that the infrared spectra assigned here to $CH_2(OH)_2$ and $POCH_2OH$ are similar to those of surface bound dioxymethylene and polyoxymethylene compounds observed when adsorbing gaseous $CH_2{=}O$ onto various porous oxides.[10,11] This is not surprising because all these species feature the same OCH_2O moiety.[12] However, the formaldehyde products observed on oxide surfaces can be distinguished from those found in the FAPO-5 sieve based on their thermal stability; the oxymethylene species formed on porous oxide surfaces are stable at room temperature, whereas $CH_2(OH)_2$ and $POCH_2$-OH quantitatively dissociate above 0 °C (see below).

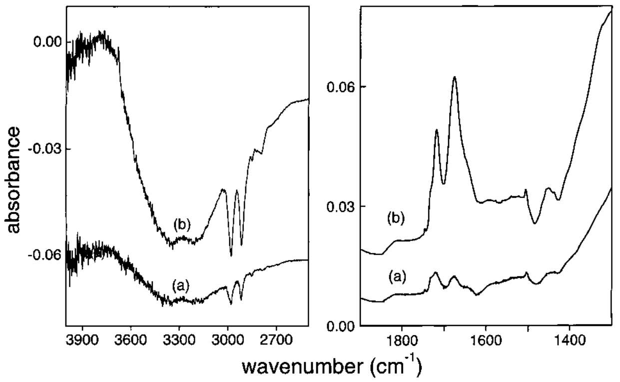

Figure 3. Thermal behavior of adducts formed upon coadsorption of $CH_2{=}O$ and H_2O in FAPO-5. Infrared difference spectra show reaction after the warming of the system displayed in Figure 2c to 296 K: (a) immediately after reaching 296 K and (b) 70 min at 296 K.

Analogous loading experiments with $CD_2{=}O$ confirmed the result with the parent reactions just described. In "dehydrated" FAPO-5 (no extra water added after evacuation at 200 °C) or in FAPO-5 loaded with an additional small amount of H_2O, both gas phase (1701 cm^{-1}) and adsorbed $CD_2{=}O$ (1685, 2091, 2213, 2256 cm^{-1}) decreased rapidly under depletion of H_2O and lattice OH groups. Product absorptions were at 2105, 2138, 2225 (shoulder), and 2254 cm^{-1}. Comparison of the product intensities at the two H_2O concentrations indicates that the 2138 and 2254 cm^{-1} peaks originate from $CD_2(OH)_2$, in good agreement with a Raman study of $CD_2(OD)_2$,[13] whereas 2105 and 2225 cm^{-1} absorptions are assigned to C−D stretching modes of $P-OCD_2OH$ groups (Table 2, column 2). The OH stretching modes of both products give rise to a broad absorption around 3200 cm^{-1}.

Warm up to 296 K of the FAPO-5 sieve containing $CH_2(OH_2)$ and $P-OCH_2OH$ led to depletion of the two adducts under release of $CH_2{=}O$ (1504, 1732 cm^{-1}). Figure 3a shows the infrared difference spectrum taken after and before raising the pellet temperature from 250 to 296 K for FAPO-5 preloaded with an additional amount of H_2O. After 70 min at 296 K, nearly quantitative conversion of $CH_2(OH)_2$ to methyl formate, HCO_2CH_3 (1717, 1456, and 1436 cm^{-1}) and HCO_2H (1679 and 1381 cm^{-1}), has occurred (Figure 3b). Assignments of these products are readily made on the basis of FT-IR measurements reported earlier for room-temperature loading of CH_2O.[1] The emergence of formaldehyde suggests that the initial step upon warm is the reverse of reactions 1 and 2 followed by Cannizzaro disproportionation:[1,14]

$$2CH_2{=}O + H_2O \rightarrow HCO_2H + CH_3OH \qquad (3)$$

We have noted previously that formic acid and methanol condense slowly to methylformate in a FAPO-5 sieve at room temperature.[1] Because the growth of HCO_2CH_3 in Figure 3 does not exhibit a clear induction period, the ester may in addition emerge from Tishchenko dimerization of formaldehyde[15,16]

$$CH_2{=}O + CH_2{=}O \rightarrow HCO_2CH_3 \qquad (4)$$

Note that a very small amount of HCO_2H is already formed upon $CH_2{=}O$ loading at 250 K (Figure 2c). However, the growth of these bands at 250 K shows a distinct induction

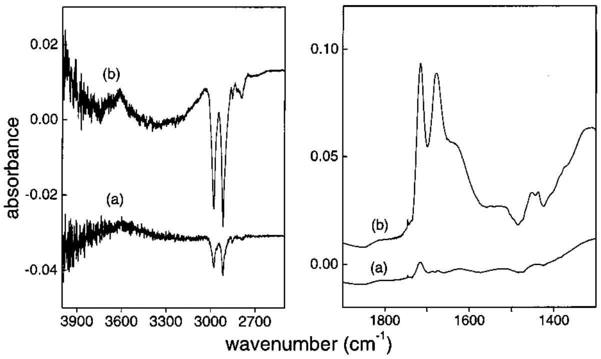

Figure 4. Thermal behavior of adducts formed upon adsorption of $CH_2{=}O$ into dehydrated FAPO-5. Infrared difference spectra show reaction following the warming of the system displayed in Figure 2b to 296 K: (a) immediately after reaching 296 K and (b) 110 min at 296 K.

period, in contrast to the $CH_2(OH)_2$ and $P{-}OCH_2OH$ absorptions. This confirms that formic acid originates from initially produced formaldehyde adducts, although at a much slower rate than at room temperature. Analogous observations were made in warm experiments of a FAPO-5 sieve containing $CD_2(OH)_2$ and $P{-}OCD_2OH$, leading to DCO_2H (1660 cm^{-1}) and DCO_2CD_3 (1685, 2075, and 2192 cm^{-1}).

A corresponding series of warm-up experiments with formaldehyde adducts in the FAPO-5 sieve with minimal H_2O content, shown in Figure 4, confirmed the observations made above. Spectra a of Figures 4 and 3 afford a comparison of the fate of $CH_2(OH)_2$ and $P{-}OCH_2OH$ in sieves with different H_2O concentration. As expected, the matrix with lower water concentration exhibits a higher $POCH_2OH/CH_2(OH)_2$ depletion ratio. This is most clearly seen when comparing the intensities of the bands at 2913 cm^{-1} ($POCH_2OH$) and 2978 cm^{-1} ($CH_2(OH)_2$). Furthermore, the HCO_2CH_3/HCO_2H product ratio (1717/1679 cm^{-1}) is higher in the matrix with less H_2O (Figure 4a), indicating that Tishchenko reaction 4 of $CH_2{=}O$ is enhanced, whereas Cannizzaro reaction 3 is diminished. The same observations are made in runs with $CD_2{=}O$ adducts. Table 3 summarizes infrared spectra of all species observed in $CH_2{=}O$ and $CD_2{=}O$ loading experiments in FAPO-5.

From this series of $CH_2{=}O$ and $CD_2{=}O$ loading experiments in a FAPO-5 sieve containing small amounts of water, we conclude that formaldehyde reacts with lattice $P{-}OH$ groups and residual H_2O to yield $P{-}OCH_2OH$ and methanediol, respectively. The addition occurs at 250 K within a few minutes or faster. Raising the temperature to 296 K results in release of formaldehyde followed by Cannizzaro and Tishchenko reactions to yield formic acid and methylformate. The rise time of these final products at room temperature is around 2 h. Irradiation of FAPO-5 containing $CH_2(OH)_2$ and $P{-}OCH_2OH$ at 250 K with 355 nm light did not accelerate the conversion to formaldehyde or carboxyl products.

Formaldehyde + H_2O_2. Exposing a room-temperature FAPO-5 pellet loaded with H_2O_2/H_2O solution according to the method described in section II to 1 Torr of $CH_2{=}O$ gas resulted in instantaneous product absorptions at 1456, 2884, and 2948 cm^{-1}, as shown in Figure 5a. The bands agree with those of a gas-phase FT-IR spectrum of HO_2CH_2OH reported by the groups of Niki and Calvert.[17,18] Therefore, we assign the product to hydroxymethylhydroperoxide formed by addition of formaldehyde to hydrogen peroxide:

$$CH_2{=}O + H_2O_2 \rightarrow HO_2CH_2OH \qquad (5)$$

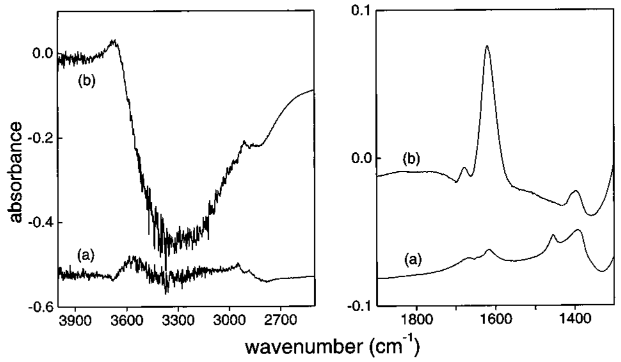

Figure 5. Infrared spectra recorded upon adsorption of 1 Torr $CH_2{=}O$ into a FAPO-5 sieve loaded with H_2O_2/H_2O solution at 296 K. (a) Difference of spectra taken after 2 min exposure to $CH_2{=}O$ and before adding formaldehyde. Intense absorption of reactant and product OH groups in the 3000−3600 cm^{-1} region prevents identification of peaks of HO_2CH_2OH. The shoulder at 1390 cm^{-1} is a baseline effect not associated with a guest absorption. (b) Difference spectra recorded upon irradiation at 355 min (500 mW cm^{-2}) for 5 min and before $CH_2{=}O$ loading.

TABLE 3: Infrared Product Frequencies upon Adsorption of Formaldehyde onto a FAPO-5 Sieve at 250 K and Warm Up to 296 K (in cm^{-1})

frequency		
$CH_2{=}O$	$CD_2{=}O$	species
1381		HCO_2H
1400		$POCH_2OH$
1422		$CH_2(OH)_2$
1436		HCO_2CH_3
1456		HCO_2CH_3
1472		$POCH_2OH$
1484		$POCH_2OH$
1503		$CH_2{=}O$
	1620	$DCO_2^-{\cdots}Fe$
1628		$HCO_2^-{\cdots}Fe$
	1660	DCO_2H
1679		HCO_2H
	1685	$CD_2{=}O$, DCO_2CD_3
1717		HCO_2CH_3
1720		$CH_2{=}O$
1732		$CH_2{=}O$
	2075	DCO_2CD_3
	2091	$CD_2{=}O$
	2106	$POCD_2OH$
	2137	$CD_2(OH)_2$
	2192	DCO_2CD_3, $DCO_2^-{\cdots}Fe$
	2213	$CD_2{=}O$
	2225	$POCD_2OH$
	2256	$CD_2{=}O$, $CD_2(OH)_2$
2795		$POCH_2OH$
2824		$CH_2{=}O$
2852		HCO_2CH_3
2898		$CH_2{=}O$
2913		$POCH_2OH$, $HCO_2^-{\cdots}Fe$
2978		$CH_2(OH)_2$
2990		$CH_2{=}O$
3200 (broad)		$CH_2(OH)_2$, $POCH_2OH$ $CD_2(OH)_2$, $POCD_2OH$

The same spectrum was observed upon synthesis of an authentic sample of HO_2CH_2OH by bubbling $CH_2{=}O$ gas through a 30% H_2O_2 solution at 60 °C for 3 h, as described in the literature,[19] followed by loading of the solution into the FAPO-5 pellet. An additional shoulder of 1677 cm^{-1} and a band at 1618 cm^{-1} indicate the spontaneous formation of small amounts of HCO_2H and $HCO_2^-{\cdots}Fe$, respectively (Figure 5a). No trace of gas phase or adsorbed $CH_2{=}O$ was detected, and no further growth of HO_2CH_2OH occurred after the initial spectrum was recorded. This implies that formaldehyde reacts substantially faster with

H_2O_2 than with H_2O or lattice OH groups, consistent with the finding that HO_2CH_2OH is formed at the exclusion of $CH_2(OH)_2$ and $POCH_2OH$ (Figure 5a). In contrast to the behavior of $CH_2(OH)_2$ or $POCH_2OH$, brief irradiation at 355 nm of FAPO-5 containing HO_2CH_2OH (5 min at 500 mW cm^{-2}) led to quantitative conversion of the hydroperoxide to HCO_2H (1677 cm^{-1}) and $HCO_2^{-}\cdots Fe$ (1618 and 2912 cm^{-1}), as can be seen from Figure 5, trace b. The 1618 cm^{-1} absorption is presumably an overlap of formate and H_2O product bands:

$$HO_2CH_2OH \xrightarrow[355\text{ nm}]{h\nu} H_2O + HCO_2H \qquad (6)$$

The simultaneous depletion at 1456, 2884, and 2948 cm^{-1} confirms the assignment of these bands to HO_2CH_2OH. In a more detailed study, we found that irradiation at 500 mW cm^{-2} for a mere 20 s led to complete depletion of HO_2CH_2OH. No bleach of $CH_2(OH)_2$, $POCH_2OH$, or CH_3OCH_2OH was detected under these photolysis conditions. Reaction 6 is the established UV photodissociation channel of hydroxymethylhydroperoxide.[20] Similar loading experiments with $CD_2{=}O$ revealed HO_2CD_2OH product absorptions at 2104 and 2256 cm^{-1}. As in the case of the parent isotope, reaction with H_2O_2 was complete on the time scale of an FT-IR run, and subsequent photolysis resulted in efficient conversion to DCO_2H (1658 cm^{-1}) and $DCO_2^{-}\cdots Fe$ (1613 and 2188 cm^{-1}). We conclude that formaldehyde reacts with H_2O_2 in a FAPO-5 sieve within less than 2 min to yield hydroxymethylhydroperoxide. The adduct rearranges thermally at room temperature to formic acid (formate) and H_2O with a decay time of about 20 min. Efficient dissociation to the same products takes place upon 355 nm irradiation.

Implications for a Mechanism of $CH_3OH + O_2$ Photooxidation. The lack of any build-up of the postulated $CH_2{=}O$ intermediate upon 355 nm induced reaction of CH_3OH with O_2 in a FAPO-5 sieve[1] might be due to rapid formation of adducts with CH_3OH, H_2O, lattice OH groups, or H_2O_2. The considerable stability of CH_3OCH_2OH (10 h), $CH_2(OH)_2$ (2 h), and $POCH_2OH$ (2 h) with respect to thermal release of formaldehyde (and subsequent Cannizzaro or Tishchenko reaction) in the room-temperature sieve rules out any significant role of these intermediates. On the other hand, HO_2CH_2OH exhibits a much shorter lifetime at room temperature (complete dissociation in 20 min) and is extremely photolabile with respect to fragmentation to HCO_2H and H_2O. Clearly, the adduct of formaldehyde and H_2O_2 might play a role as an intermediate of the $CH_3OH + O_2$ photoreaction in FAPO-5 sieve. Time-resolved FT-IR spectroscopy is required to investigate this possibility.[21]

IV. Conclusions

In this paper, we have studied the reactivity of gaseous formaldehyde in the pores of an Fe aluminophosphate sieve (AFI structure) with H_2O, H_2O_2, CH_3OH, or lattice OH groups. These molecules are present in the reaction mixture of LMCT-induced $CH_3OH + O_2$ photooxidation in a FAPO-5 sieve and could therefore act as chemical traps of formaldehyde, a proposed intermediate. Infrared spectra of all four addition products, namely, $CH_2(OH)_2$, HO_2CH_2OH, CH_3OCH_2OH, and $POCH_2OH$, as well as partially deuterated modifications have been established. Knowledge of infrared absorptions of these species is crucial for analyzing mechanistic experiments based on time-resolved FT-IR spectroscopy of $CH_3OH + O_2$ photooxidation in this framework substituted transition metal sieve. Among the formaldehyde reaction products, hydroxymethylhydroperoxide, the adduct of $CH_2{=}O$ and H_2O_2, exhibits thermal and photodissociation behavior consistent with a role in the LMCT-induced photoreaction of CH_3OH and O_2 in an Fe aluminophosphate sieve.

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