

Figure 4. Thermal behavior of adducts formed upon adsorption of $\text{CH}_2=\text{O}$ 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 $\text{CH}_2(\text{OH})_2$ and $\text{P}-\text{OCH}_2\text{OH}$ 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 $\text{CD}_2(\text{OH})_2$ and $\text{P}-\text{OCD}_2\text{OH}$, leading to DCO_2H (1660 cm^{-1}) and $\text{DCO}_2\text{-CD}_3$ (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 $\text{CH}_2(\text{OH})_2$ and $\text{P}-\text{OCH}_2\text{OH}$ in sieves with different H_2O concentration. As expected, the matrix with lower water concentration exhibits a higher $\text{POCH}_2\text{OH}/\text{CH}_2(\text{OH})_2$ depletion ratio. This is most clearly seen when comparing the intensities of the bands at 2913 cm^{-1} (POCH_2OH) and 2978 cm^{-1} ($\text{CH}_2(\text{OH})_2$). Furthermore, the $\text{HCO}_2\text{CH}_3/\text{HCO}_2\text{H}$ product ratio ($1717/1679\text{ cm}^{-1}$) is higher in the matrix with less H_2O (Figure 4a), indicating that Tishchenko reaction 4 of $\text{CH}_2=\text{O}$ is enhanced, whereas Cannizzaro reaction 3 is diminished. The same observations are made in runs with $\text{CD}_2=\text{O}$ adducts. Table 3 summarizes infrared spectra of all species observed in $\text{CH}_2=\text{O}$ and $\text{CD}_2=\text{O}$ loading experiments in FAPO-5.

From this series of $\text{CH}_2=\text{O}$ and $\text{CD}_2=\text{O}$ loading experiments in a FAPO-5 sieve containing small amounts of water, we conclude that formaldehyde reacts with lattice $\text{P}-\text{OH}$ groups and residual H_2O to yield $\text{P}-\text{OCH}_2\text{OH}$ 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 $\text{CH}_2(\text{OH})_2$ and $\text{P}-\text{OCH}_2\text{OH}$ 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 $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solution according to the method described in section II to 1 Torr of $\text{CH}_2=\text{O}$ 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 $\text{HO}_2\text{CH}_2\text{OH}$ 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:

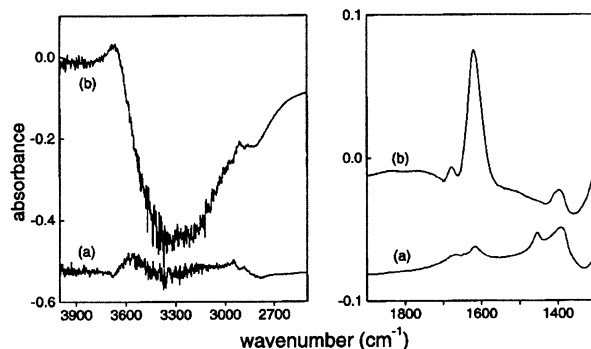
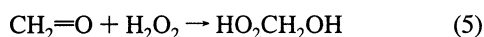


Figure 5. Infrared spectra recorded upon adsorption of 1 Torr $\text{CH}_2=\text{O}$ into a FAPO-5 sieve loaded with $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ solution at 296 K. (a) Difference of spectra taken after 2 min exposure to $\text{CH}_2=\text{O}$ and before adding formaldehyde. Intense absorption of reactant and product OH groups in the $3000\text{--}3600\text{ cm}^{-1}$ region prevents identification of peaks of $\text{HO}_2\text{CH}_2\text{OH}$. 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 $\text{CH}_2=\text{O}$ 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		species
$\text{CH}_2=\text{O}$	$\text{CD}_2=\text{O}$	
1381		HCO_2H
1400		POCH_2OH
1422		$\text{CH}_2(\text{OH})_2$
1436		HCO_2CH_3
1456		HCO_2CH_3
1472		POCH_2OH
1484		POCH_2OH
1503		$\text{CH}_2=\text{O}$
	1620	$\text{DCO}_2\cdots\text{Fe}$
1628		$\text{HCO}_2\cdots\text{Fe}$
	1660	DCO_2H
1679		HCO_2H
	1685	$\text{CD}_2=\text{O}$, DCO_2CD_3
1717		HCO_2CH_3
1720		$\text{CH}_2=\text{O}$
1732		$\text{CH}_2=\text{O}$
	2075	DCO_2CD_3
	2091	$\text{CD}_2=\text{O}$
	2106	POCH_2OH
	2137	$\text{CD}_2(\text{OH})_2$
	2192	DCO_2CD_3 , $\text{DCO}_2\cdots\text{Fe}$
	2213	$\text{CD}_2=\text{O}$
	2225	POCH_2OH
	2256	$\text{CD}_2=\text{O}$, $\text{CD}_2(\text{OH})_2$
2795		POCH_2OH
2824		$\text{CH}_2=\text{O}$
2852		HCO_2CH_3
2898		$\text{CH}_2=\text{O}$
2913		POCH_2OH , $\text{HCO}_2\cdots\text{Fe}$
2978		$\text{CH}_2(\text{OH})_2$
2990		$\text{CH}_2=\text{O}$
3200 (broad)		$\text{CH}_2(\text{OH})_2$, POCH_2OH $\text{CD}_2(\text{OH})_2$, POCH_2OH

The same spectrum was observed upon synthesis of an authentic sample of $\text{HO}_2\text{CH}_2\text{OH}$ by bubbling $\text{CH}_2=\text{O}$ gas through a 30% H_2O_2 solution at $60\text{ }^\circ\text{C}$ 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 $\text{HCO}_2\cdots\text{Fe}$, respectively (Figure 5a). No trace of gas phase or adsorbed $\text{CH}_2=\text{O}$ was detected, and no further growth of $\text{HO}_2\text{CH}_2\text{OH}$ occurred after the initial spectrum was recorded. This implies that formaldehyde reacts substantially faster with