

Chemical Reactivity of Formaldehyde in a FeAlPO₄ Sieve[†]

Y. H. Yeom, N. Ulagappan, and H. Frei*

Physical Biosciences Division, Calvin Laboratory, Lawrence Berkeley National Laboratory,
University of California, Berkeley, California 94720

Received: March 20, 2001

Formaldehyde gas loaded into a framework Fe aluminophosphate sieve (FeAlPO₄-5) at 250 K was found to react with adsorbed H₂O, CH₃OH, H₂O₂, or lattice OH groups to yield the corresponding addition products, namely, CH₂(OH)₂, CH₃OCH₂OH, HO₂CH₂OH, or POCH₂OH, respectively. Reactions were monitored *in situ* by static FT-IR spectroscopy, and assignments are based on experiments with CD₂=O and CD₃OD. Most efficient was the reaction with H₂O₂, as indicated by the fact that HO₂CH₂OH was formed at the exclusion of CH₂(OH)₂ and POCH₂OH when adsorbing formaldehyde onto a sieve loaded with H₂O₂ and H₂O. Methoxymethanol, methanediol, and POCH₂OH 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 FeAlPO₄ sieve, HO₂CH₂OH 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 FeAlPO₄-5 (abbreviated FAPO-5) molecular sieve.¹ The material consists of a one-dimensional system of 7.3 Å diameter channels.² O₂ was used as electron acceptor, and methanol was used as a donor. Formic acid (formate), H₂O, and methyl formate were observed as final products, the latter emerging from a slow ester condensation of HCO₂H and excess CH₃OH. Formaldehyde and H₂O₂ 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 CH₃OH, framework OH groups, or coproducts H₂O₂ or H₂O. To find out about the formation of such adducts and their possible role in the CH₃OH+O₂ 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 CH₃OH+O₂ 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 CaF₂ 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-D₄ (Aldrich, 99% D) were degassed by freeze–pump–thaw cycles before use. Formaldehyde gas was obtained by depolymerization of paraformaldehyde (Aldrich, 95%) or deuterio 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 H₂O₂/H₂O 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 CH₃OH 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 CH₂=O resulted in instantaneous depletion of methanol under concurrent formation of a product whose infrared spectrum is shown in Figure

[†] Part of the special issue “Mitsuo Tasumi Festschrift”.

* To whom correspondence should be addressed.