# **Inorganic Chemistry**

# Nucleophilic versus Electrophilic Activation of Hydrogen Peroxide over Zr-Based Metal–Organic Frameworks

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# ACCESSImage: Metrics & MoreImage: Article RecommendationsImage: Supporting InformationABSTRACT: Zr-based metal-organic frameworks (Zr-MOF) UiO-66<br/>and UiO-67 catalyze thioether oxidation in nonprotic solvents with<br/>unprecedentedly high selectivity toward corresponding sulfones (96- $H_2O_2$ (1 equiv.)<br/> $H_2O_2$

99% at ca. 50% sulfide conversion with only 1 equiv of  $H_2O_2$ ). The reaction mechanism has been investigated using test substrates, kinetic, adsorption, isotopic (<sup>18</sup>O) labeling, and spectroscopic tools. The following facts point out a nucleophilic character of the peroxo species responsible for the superior formation of sulfones: (1) nucleophilic parameter  $X_{Nu} = 0.92$  in the oxidation of thianthrene 5-oxide and its decrease upon addition of acid; (2) sulfone to sulfoxide ratio of 24 in the competitive oxidation of methyl phenyl sulfoxide and *p*-Br-methyl phenyl sulfide; (3) significantly lower initial rates of methyl phenyl sulfide oxidation relative to methyl phenyl sulfoxide ( $k_S/k_{SO} = 0.05$ ); and



(4) positive slope  $\rho = +0.42$  of the Hammett plot for competitive oxidation of *p*-substituted aryl methyl sulfoxides. Nucleophilic activation of H<sub>2</sub>O<sub>2</sub> on Zr-MOF is also manifested by their capability of catalyzing epoxidation of electron-deficient C==C bonds in  $\alpha$ , $\beta$ -unsaturated ketones accompanied by oxidation of acetonitrile solvent. Kinetic modeling on methyl phenyl sulfoxide oxidation coupled with adsorption studies supports a mechanism that involves the interaction of H<sub>2</sub>O<sub>2</sub> with Zr sites with the formation of a nucleophilic oxidizing species and release of water followed by oxygen atom transfer from the nucleophilic oxidant to sulfoxide that competes with water for Zr sites. The nucleophilic peroxo species coexists with an electrophilic one, ZrOOH, capable of oxygen atom transfer to nucleophilic sulfides. The predominance of nucleophilic activation of H<sub>2</sub>O<sub>2</sub> over electrophilic one is, most likely, ensured by the presence of weak basic sites in Zr-MOFs identified by FTIR spectroscopy of adsorbed CDCl<sub>3</sub> and quantified by adsorption of isobutyric acid.

#### ■ INTRODUCTION

Metal-organic frameworks (MOFs) have attracted a great deal of research interest owing to a unique ensemble of properties, such as inherent hybrid nature, crystalline open structures, extraordinarily high surface areas, and content of uniform and accessible metal sites. Their remarkable synthetic tunability allows for chemical and physical properties to be adapted to targeted applications, including gas storage, separation, molecular recognition, biomedicine, sensing, and heterogeneous catalysis.<sup>1–11</sup> Zr-MOFs constructed from very robust Zr<sub>6</sub>-oxohydroxo clusters and various carboxylate linkers remain one of the most appealing classes of MOFs because of their outstanding chemical, thermal, hydrothermal, and mechanical stability.<sup>12–19</sup> In particular, the member of the UiO family (UiO stands for University of Oslo), UiO-66 constituted by  $Zr_6O_4(OH)_4$  nodes connected by maximally 12 terephthalates or 1,4-benzenedicarboxylate (BDC) ligands, withstands temperature up to 350-450 °C under air and tolerates a broad range of solvents and reagents.<sup>14–16,19</sup>

In recent years, UiO-66 was found to be an active and recyclable catalyst for a variety of catalytic transformations, most of which belong to acid—base catalysis.<sup>17,19–28</sup> Numerous studies have shown that the catalytic activity of UiO-66 and other MOFs can be greatly enhanced through the generation of defect (open) sites in their crystalline structure.<sup>10,11,19,22,29–31</sup> Initially, Lewis acid sites (LAS) created by linker defects were suggested to be responsible for the catalytic activity of UiO-66,<sup>22,23,26,32</sup> sometimes in cooperation with Lewis basic sites (e.g., amine groups) present in a functionalized linker.<sup>20,25,28</sup> However, more recent studies implied that the high potential of UiO-66 and related materials as catalysts is, most likely, due to

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their dual acid/base character and cooperative work of Lewis and Brønsted sites.  $^{27,33-35}$ 

To date, the catalytic performance of Zr-MOFs, including UiO-66 (without any MOF modification with other transition metals), in oxidation catalysis has been much less explored, <sup>36–42</sup> although UiO-66 demonstrated fairly good stability in the presence of aqueous  $H_2O_2$ .<sup>16</sup> The majority of publications deal with oxidations of S-compounds, notably oxidative desulfurization of thiophenes<sup>36–38</sup> with aqueous  $H_2O_2$  as oxidant. It was proposed that the catalytic activity of UiO-66 in the oxidation of S-compounds correlates with the number of missing-linker defects<sup>36,38</sup> and accessible "open" sites<sup>39</sup> in the crystalline structure. Importantly, it was also demonstrated that the  $H_2O_2$ -based oxidation catalysis over UiO-66 has a truly heterogeneous nature, that is, the reaction occurs on the catalyst surface and is not due to Zr species leached into solution.<sup>36</sup>

Very few attempts were undertaken to unravel the mechanisms of  $H_2O_2$  activation and oxygenation reactions over Zr-MOFs. Nguyen and co-workers investigated the oxidation of methyl phenyl sulfide (MPS) by kinetic and computational tools and suggested that both MPS and corresponding sulfoxide involves  $Zr-\mu^1$ -OOH active intermediates formed at defect open sites of UiO-66.<sup>39</sup> A predomination of sulfone over sulfoxide, observed in MeCN and CH<sub>2</sub>Cl<sub>2</sub> solvents, was rationalized in the framework of a model where sulfoxide product binds to a site adjacent to the active  $Zr-\mu^1$ -OOH species, resulting in a higher degree of over-oxidation through increased local concentration.<sup>39</sup> However, Zheng et al. suggested that homolytic decomposition of H<sub>2</sub>O<sub>2</sub> producing OH radicals is responsible for the oxidative desulfurization of dibenzothiophene over Zr-MOFs.<sup>41</sup>

Recently, we have found a remarkable effect of acid additives on the selectivity of  $H_2O_2$ -based oxidation of cyclohexene over Zr-MOFs (UiO-66, UiO-67, and MOF-801), which is not accompanied by alterations in the MOF structure and formation of new defects.<sup>42</sup> It was demonstrated that protons facilitate heterolytic activation of the oxidant and prevent its unproductive degradation on Zr-MOFs, thereby leading to selective oxygenation of the C=C bond without oxidation of the allylic C-H bonds via a homolytic mechanism.

So far, the question about the nature of the reactivity and electronic character of the active peroxo species operating in Zr-MOFs was not addressed, though understanding this is the key to understanding the origin of selectivity. Motivated by this knowledge gap, we investigated the mechanism of the oxidation of S-compounds using a methodology that involves competitive sulfide-sulfoxide oxidation experiments, product analysis on the probe substrate thianthrene 5-oxide, and Hammett correlations, along with kinetic, isotopic, and spectroscopic tools. The results acquired in this work unambiguously indicate a predominantly nucleophilic character of the oxidizing species formed upon the interaction of H<sub>2</sub>O<sub>2</sub> and Zr-MOF in nonprotic solvents and responsible for the highly selective formation of sulfones. A capability of the catalyst system UiO-66(67)/H<sub>2</sub>O<sub>2</sub>/MeCN to perform epoxidation of electron-deficient C=C bonds in unsaturated ketones also supports this suggestion. FTIR spectroscopic techniques with CDCl<sub>3</sub> as a probe molecule and adsorption of isobutyric acid were employed to evaluate the presence of basic sites in UiO-66 that might be responsible for the nucleophilic activation of hydrogen peroxide. To the best of our knowledge, this is the first report that describes the capability of MOFs for the formation of a nucleophilic oxidant from  $H_2O_2$ .

#### EXPERIMENTAL SECTION

Instrumentation. GC analyses were performed using a gas chromatograph Chromos GC-1000 equipped with a flame ionization detector and a quartz capillary column BPX5 (30 m × 0.25 mm). GC-MS analyses were carried out using an Agilent 7000B system with the triple-quadrupole mass-selective detector Agilent 7000 (ZB-Wax, 25 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). HPLC measurements were performed using HPLC Agilent Technologies 1220 Infinity LC using ZORBAX Eclipse Plus C-18 column ( $4.6 \times 150$  mm, 5-Micron, H<sub>2</sub>O-*i*PrOH = 40:60 (for MPS conversion) or  $H_2O-MeCN = 40.60$  (for MPSO<sub>2</sub> yield), 1 mL/ min, 25 °C). <sup>1</sup>H NMR spectra were recorded at 400.130 MHz on a Brüker AVANCE-400 spectrometer. X-ray diffraction patterns were collected on the Siemens D500 instrument using Cu K $\alpha$  radiation. Infrared spectra of 0.5–2.0 wt % samples in KBr pellets were recorded on an Agilent Cary 660 FTIR spectrometer. Infrared spectra of adsorbed CO and CDCl<sub>3</sub> were recorded on a Shimadzu IRTracer-100 spectrometer. The Raman spectrometer T64000 (Horiba Jobin Yvon) with the micro-Raman setup was used to measure the Raman spectra. All experimental spectra were collected in the backscattering geometry using the 514.5 nm line of an Ar<sup>+</sup> laser. The spectral resolution was not worse than 1.5 cm<sup>-1</sup>. The detector was a silicon-based CCD matrix and cooled with liquid nitrogen. The power of the laser beam reaching the sample was 2 mW. The band at 520.5 cm<sup>-1</sup> of Si single crystal was used to calibrate the spectrometer. Scanning electron microscopy (SEM) images were acquired by means of a JEOL JSM-6460 LV microscope. Thermogravimetric analysis (TGA) was carried out in airflow (30 mL/ min) using a NETZSCH STA 449C instrument. The sample weight was 10 mg in all experiments and the heating rate in TG experiment was 5 °C/min.

Zr-MOF Synthesis and Characterization. UiO-66 was synthesized from zirconyl chloride and H<sub>2</sub>BDC by a solvothermal method following the procedure reported by Ragon et al.43 with some modifications (see the Supporting Information for details). UiO-67 was prepared from zirconium chloride and 4,4'-biphenyldicarboxylic acid (H<sub>2</sub>BPDC) according to the protocol described by Katz et al.<sup>44</sup> The structure of UiO-66 and UiO-67 was confirmed by XRD (Figures S1 and S2, respectively), FT-IR spectroscopy (Figure S3), and N<sub>2</sub> adsorption (Table S1). SEM and TEM measurements (Figure S4) revealed that the UiO-66 solid consisted of very small particles (ca. 20 nm), while UiO-67 had larger particles (ca. 200 nm). According to TGA measurements (Figure S5), the structure of UiO-66 and UiO-67 samples comprised missing linker defects (10.8 BDC and 10.0 BPDC, respectively, instead of 12 in the ideal structure). Cluster  $[Zr_6O_4(OH)_4(OAc)_{12}]_2$  (Zr<sub>6</sub>)<sub>2</sub> was synthesized by reacting ZrOCl<sub>2</sub>. 8H<sub>2</sub>O with acetic acid under solvothermal conditions.<sup>45</sup>

**Catalytic Oxidation of S-Compounds.** Catalytic reactions were performed under vigorous stirring (500 rpm) in thermostat-equipped glass vessels. Each experiment was reproduced 2–3 times. Reactions of MPS oxidation were initiated by addition of  $H_2O_2$  (0.1 mmol) to a solution of MPS (0.1 M) in 1 mL of solvent (typically, MeCN) at 27 °C containing 2 mg of UiO-66 or 2.4 mg of UiO-67 (7  $\mu$ mol Zr). The oxidation products were identified by the comparison of GC retention time with the retention time of the authentic samples and by GC-MS analysis. MPS conversion and product yields were quantified by GC using biphenyl as internal standard.

Oxidation of thianthrene oxide (SSO) was performed at 27 °C by addition of  $H_2O_2$  (0.05 mmol) to a mixture of SSO (0.05 mmol), UiO-66 (1 mg), and MeCN (2 mL). After 24 h, the catalyst was filtered off, the solvent was evaporated, and CDCl<sub>3</sub> was added to the solid to dissolve the probe for <sup>1</sup>H NMR analysis of the reaction products. SSO conversion and product yields were calculated by the integration of corresponding signals in the <sup>1</sup>H NMR spectra, considering that the total amount of all products is 100%.

**Catalytic Oxidation of**  $\alpha$ , $\beta$ **-Unsaturated Ketones.** Oxidation of unsaturated carbonyl compounds was carried out at 70 °C. H<sub>2</sub>O<sub>2</sub> (0.8 mmol) was added to a mixture containing substrate (0.1 mmol), UiO-66(67) (5 mg), and 1 mL of solvent (MeCN or EtOAc). The reaction products were identified by GC-MS. Substrate conversions and product yields were determined by GC using biphenyl as internal standard.

Table 1. Catalytic Oxidation of MPS with  $H_2O_2$  in the Presence of Zr-MOFs<sup>a</sup>

|                |                   | MPS     | $H_2O_2$<br>$7 \circ C$ $MPSO$ $O$ $S$ $MPSO$ | Zr-MOF/H <sub>2</sub> O <sub>2</sub> |           |                         |
|----------------|-------------------|---------|---|--------------------------------------|-----------|-------------------------|
|                |                   |         |   |                                      | product y | rields (%) <sup>c</sup> |
| entry          | catalyst          | solvent | time $(h)^{b}$                                | MPS conversion (%)                   | MPSO      | MPSO <sub>2</sub>       |
| 1              | UiO-66            | MeCN    | 0.25  | 49                                   | 0.5 (1)   | 48.5 (99)               |
| 2              | $UiO-66 + H^{+d}$ | MeCN    | 3.5   | 59                                   | 19 (32)   | 40 (68)                 |
| 3              | UiO-66            | DMC     | 0.5   | 51                                   | 1 (2)     | 50 (98)                 |
| 4              | UiO-66            | EtOAc   | 1   | 51                                   | 2 (4)     | 49 (96)                 |
| 5              | UiO-66            | MeOH    | 2   | 52                                   | 16 (31)   | 36 (69)                 |
| 6 <sup>e</sup> | UiO-66            | MeCN    | 0.25  | 48                                   | 4 (8)     | 44 (92)                 |
| 7              | UiO-67            | MeCN    | 0.5   | 51                                   | 2 (4)     | 49 (96)                 |
| 8              | $(Zr_6)_2$        | MeCN    | 2   | 50                                   | 6 (12)    | 44 (88)                 |
| 9              | no catalyst       | MeCN    | 24  | 14                                   | 11 (79)   | 3 (21)                  |

<sup>*a*</sup>Reaction conditions: MPS 0.1 mmol,  $H_2O_2$  0.1 mmol, Zr-MOF 1.9 mg of  $(Zr_6)_2$  or 2 mg of UiO-66 or 2.4 mg of UiO-67, MeCN 1 mL, 27 °C. <sup>*b*</sup>Time of reaching maximum MPS conversion, except for Entry 9, where the reaction was very slow. 'Yield based on initial MPS. Selectivity is given in parentheses. <sup>*d*</sup>7 µmol of HClO<sub>4</sub> were added (corresponds to 1 equiv. relative to Zr). <sup>*e*</sup>Urea-H<sub>2</sub>O<sub>2</sub> was used instead of aqueous H<sub>2</sub>O<sub>2</sub>.

**Competitive Oxidation of Br-MPS and MPSO.** To initiate the reaction, 0.0125 mmol of  $H_2O_2$  were added to a mixture of Br-MPS (0.1 mmol), MPSO (0.1 mmol), and UiO-66 (2 mg) in MeCN (1 mL) at room temperature. Consumption of Br-MPS and MPSO and product yields were determined by GC.

**Competitive Oxidation of Et<sub>2</sub>S and MPS.**  $H_2O_2$  (0.2 mmol) was added to a solution of Et<sub>2</sub>S (0.1 mmol), MPS (0.1 mmol), and UiO-66 (2 mg) in 1 mL of MeCN at 27 °C. Et<sub>2</sub>S and MPS consumption and product yields were determined by GC.

**Oxidation of Benzyl Phenyl Sulfide (BPS).**  $H_2O_2$  (0.1 mmol) was added to a solution of BPS (0.1 mmol) and UiO-66 (4 mg) or  $(THA)_3[PO_4\{WO(O_2)_2\}_4]$  (0.001 mmol, THA = tetrahexylammonium) in 1 mL of MeCN at 27 °C. The oxidation products were determined by GC and GC-MS.

**Hammett Correlations.** The reaction was started by the addition of  $H_2O_2$  (0.1 or 0.2 mmol) to a mixture of sulfoxides or sulfides (H–, CH<sub>3</sub>–, CH<sub>3</sub>O–, NO<sub>2</sub>–, 0.1 mmol each) and UiO-66 (2 mg) in 1 mL of MeCN at room temperature. For oxidation of sulfoxides,  $k_X/k_H$  were calculated from final concentrations of X–MPSO and H–MPSO according to the equation:  $k_X/k_H = \{ln([p-X-MPSO]/[p-X-MPSO]_0)\}/\{ln([p-H–MPSO]/[p-H–MPSO]_0)\}$ . For oxidation of sulfides, the values of  $Wx/W_H$  were calculated from initial rates of X–MPS and H–MPS oxidation to X–MPSO and H–MPSO, respectively, determined from the reaction profiles at low conversions. Substrate conversions were determined by GC using biphenyl as internal standard. Reaction samples were treated with PPh<sub>3</sub> prior to analyses to reduce unreacted  $H_2O_2$ .

Kinetic Studies. Kinetic experiments were performed in temperature-controlled glass vessels under vigorous stirring (600 rpm). The reactions of MPS oxidation were initiated by the addition of H<sub>2</sub>O<sub>2</sub> (0.02-0.2 M) to a mixture of MPS (0.01-0.1 M), UiO-66 (0.5-5 mg), and  $H_2O$  (0.09–0.7 M) in MeCN at 27 °C. The total reaction volume was 5 mL. To determine the reaction order in  $H_2O_{2}$ , corresponding amounts of water were added to keep the H<sub>2</sub>O concentration constant (0.7 M). Oxidations of MPSO were initiated by addition of H2O2 (0.01-0.075 M) into a mixture of MPSO (0.01-0.1 M), UiO-66 (1-10 mg), and H<sub>2</sub>O (0.09-0.9 M) in MeCN (5 mL total) at 0 °C. Arrhenius activation energies were determined in the temperature ranges of 27-80 °C and 0-50 °C for MPS and MPSO oxidations, respectively. Samples of the reaction mixture were taken periodically, and MPS or MPSO consumption was determined by either GC after treatment of the reaction sample with PPh<sub>3</sub> or by HPLC. Both methods gave coincident results.

The initial rate method was employed to determine the reaction orders. Initial rates were calculated as d[Sub]/dt at t = 0, where [Sub] is

[MPS] or [MPSO]. The procedure for calculation of the initial rates was reported earlier.  $^{46,47}$ 

**Kinetic Modeling.** All kinetic curves of sulfoxide consumption were fitted simultaneously by numerically integrated MPSO concentration. A similar approach was recently employed to obtain parameters of Fenton system.<sup>48</sup> The integration was done in accordance with the system of ordinary differential equations (ODE) which corresponds to the proposed oxidation mechanism. More details on the kinetic modeling procedure along with fitting details can be found in the Supporting Information.

**Adsorption Studies.** Measurements of MPS, MPSO, and MPSO<sub>2</sub> adsorption on UiO-66 from MeCN or MeCN–H<sub>2</sub>O (0.125 M H<sub>2</sub>O) were performed following the previously reported methodology.<sup>49</sup> All experiments were carried out at room temperature (25 °C). A concentrated (2.0 M) solution of MPSO (MPS or MPSO<sub>2</sub>) was added by portions (25  $\mu$ L) to a solution containing 2 mL of MeCN or MeCN–H<sub>2</sub>O, 10  $\mu$ L of *n*-octane (internal standard), and 20 mg of UiO-66. After the addition of each portion, the mixture was stirred for 10 min. The solid was separated by centrifugation (6000 rpm, 15 min), and the concentration of MPSO (MPS or MPSO<sub>2</sub>) was determined by GC (3–5 measurements). In parallel, blank experiments (without MOF) were performed.

 $H_2^{18}O$  Labeling Experiments. Oxidation of MPS in the presence of  $H_2^{18}O$  was performed at 27 °C by the addition of nonaqueous urea–  $H_2O_2$  (0.1 mmol) to a mixture containing MPS (0.1 M), UiO-66 (2 mg), and  $H_2^{18}O$  (0.36 M) in 1 mL of MeCN. The oxidation products were analyzed by GC-MS.

**Raman Study of H<sub>2</sub>O<sub>2</sub> Interaction with UiO-66 and (Zr<sub>6</sub>)<sub>2</sub>.** An aqueous solution of hydrogen peroxide (200–400  $\mu$ L, 33 wt %) was added to a suspension of either UiO-66 (20 mg) or (Zr<sub>6</sub>)<sub>2</sub> (20 mg, 7.2  $\mu$ mol) in 10 mL of acetonitrile under stirring at room temperature. After 15 min, the powder of UiO-66 or (Zr<sub>6</sub>)<sub>2</sub> was separated by filtration, washed with acetonitrile (in some cases), and then quickly dried under a stream of argon followed by immediate collecting Raman spectra.

IR Spectroscopy with Adsorption of Probe Molecules. FTIR spectra before and after the adsorption of probe molecules (CO, CDCl<sub>3</sub>) were registered using Shimadzu IRTracer-100 spectrometer in the range of 400–6000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and accumulation of 200 scans. Self-supporting pellets (ca. 20 mg/cm<sup>2</sup>) were prepared from the sample powder, placed in an IR cell, and atmosphere evacuated at 150 °C for 1 h. CO was adsorbed at –196 °C, and a pressure varied from 0.1 to 10 Torr. CDCl<sub>3</sub> was adsorbed at 20 °C by injecting a portion of 5000  $\mu$ mol/g into the cell. A full description of the methodology used for estimation of the strength of Brønsted acid

sites (BAS) as well as strength and amount of basic sites can be found in the Supporting Information.

**Basicity Measurements.** Evaluation of the number of basic sites in Zr-MOFs was performed following a methodology similar to that reported by Carniti et al.<sup>50</sup> using isobutyric acid (IBA) as acidic probe and *n*-hexane as solvent (see Supporting Information for details). Prior to measurements, the samples were activated in vacuum at 150 °C for 3 h. The number of basic sites was determined from adsorption isotherms as the end of strong adsorption of IBA, that is, at the point where a detectable concentration of IBA appeared in the solution.

#### RESULTS AND DISCUSSION

Effects of Solvent Nature and Acid Additives on MPS Oxidation over Zr-MOFs. The oxidation of MPS with 1 equiv of  $H_2O_2$  in the presence of UiO-66 as catalyst produced the corresponding sulfone with unprecedentedly high selectivity in MeCN (99% at 49% substrate conversion; Table 1, entry 1). A hot filtration test revealed the truly heterogeneous nature of the catalysis in these conditions (Figure S8). Similar results with the superior formation of sulfone were obtained in dimethyl carbonate (DMC) and ethyl acetate (EtOAc) (Table 1, entries 3 and 4). The reaction was completed within 0.25-1 h at nearly room temperature, and the oxidant utilization efficiency was as high as 98-99%. The excellent selectivity based on the oxidant implies that unproductive homolytic decomposition of H<sub>2</sub>O<sub>2</sub> over UiO-66 is negligible during the reaction course. Replacement of aqueous  $H_2O_2$  with its anhydrous form, urea-H<sub>2</sub>O<sub>2</sub>, slightly increased the yield of sulfoxide, but sulfone remained the principal oxidation product (Table 1, entry 6), which indicates that the presence of water is not critical for sulfone selectivity.

The larger pore UiO-67 (an average pore aperture diameter of 8 Å vs 6 Å in UiO-66) also showed excellent sulfone selectivity but a slightly lower oxidation rate (Table 1, compare entries 1 and 7). We propose that one of the possible reasons for the lower activity of UiO-67, in spite of the larger pores and number of missing linkers (see Supporting Information) in this material, might be notably bigger particles (in average, 200 vs 20 nm for UiO-66; Figure S4), resulting in diffusion limitations. Given that the UiO-66 and UiO-67 samples used in this work differed significantly in their crystallinity, particle size, and defectiveness, it becomes evident that the high sulfone selectivity is an intrinsic property of the MOFs studied, regardless of their structural and morphological features. A similar conclusion could be made on the basis of the results of Granadeiro and co-workers who compared the catalytic activity of UiO-66 samples prepared by different methods and having different crystallinity in the oxidative desulfurization of fuel.<sup>3</sup>

The oxo-hydroxo cluster  $(Zr_6)_2$  also produced sulfone as the principal oxidation product (Table 1, entry 8) although the reaction rate and selectivity were lower relative to those of Zr-MOFs. Given that the structure of the  $Zr_6$  moiety is similar to the structure of inorganic secondary building units of Zr-MOFs,<sup>45</sup> we may suggest that the lower activity of the  $(Zr_6)_2$  cluster is due to the relatively low lability of the terminal acetate ligands under the reaction conditions. Moreover, the superior activity and selectivity of Zr-MOFs may be a consequence of the confinement effect. Importantly, the reaction was very slow, and sulfoxide predominated over sulfone if no catalyst was employed (Table 1, entry 9).

It is widely accepted that thioethers as strong nucleophiles can be oxidized to corresponding sulfoxides by electrophilic oxidants, while sulfoxides have biphilic nature and can interact with both electrophilic and nucleophilic oxidants to form

sulfones.<sup>51-63</sup> The extraordinarily high selectivity to sulfone in the MPS oxidation with only 1 equiv of H<sub>2</sub>O<sub>2</sub> observed for UiO-66(67) implies a much higher rate of sulfoxide oxidation relative to the parent sulfide and points out a nucleophilic oxygen transfer mechanism, which is not very common in catalysis with hydrogen peroxide. In fact, peroxo complexes of d<sup>0</sup> transition metals, such as Ti(IV), V(V), Mo(VI), and W(VI), usually behave as strong electrophiles and exhibit high selectivity to sulfoxides.<sup>52–55,63–67</sup> Nucleophilic oxygen transfer is usually associated with basic conditions<sup>51,64,68</sup> or peroxo complexes of Pt and Pd.<sup>64,69–72</sup> Nucleophilic oxidation of S-compounds was implicated for carbonyl oxide,<sup>60</sup> sodium perborate,<sup>62</sup> <sup>t</sup>BuOOH/  $Al_2O_{34}$ Some complexes of Ti(IV) and Zr(IV) revealed a biphilic nature, behaving as electrophilic oxidants toward sulfides and nucleophilic ones toward sulfoxides.<sup>74</sup> Kinetic and product studies implemented on thioether oxidation catalyzed by zirconium oxo-hydroxo clusters allowed the authors to suggest an electron-rich character of the active peroxo species.<sup>75</sup> In a few cases, sulfoxide binding to an active site was suggested to favor nucleophilic oxidation process.57,61,74

The addition of acid in the amount of 1 equiv relative to Zr increased the yield of sulfoxide relative to sulfone (Table 1, compare entries 1 and 2), which may be considered as an indication of a mechanistic shift from nucleophilic oxidation toward electrophilic one. Interestingly, a similar effect on the reaction rate and selectivity was produced by the protic solvent MeOH (Table 1, entry 5). Possible reasons for that will be discussed in the final section of the Results and Discussion.

To verify our hypothesis about the preferably nucleophilic character of the peroxo species generating in UiO-66 in the absence of acid additives or alcoholic solvents, the mechanism of UiO-66-catalyzed oxidation of S-compounds with  $H_2O_2$  was further investigated using a conventional methodology that involves product studies on the test substrate thianthrene 5-oxide, competitive experiments, and Hammett correlations.

**Oxidation of Thianthrene 5-Oxide.** After the pioneering work of Adam et al.<sup>76</sup> thianthrene 5-oxide (SSO) was widely used as a mechanistic probe for differentiating between nucleophilic and electrophilic oxidation.<sup>61,62,65–67,77–79</sup> As SSO molecule possesses both a nucleophilic sulfide and an electrophilic sulfoxide site, predomination of thianthrene 5,10-dioxide (SOSO) or thianthrene 5,5-dioxide (SSO<sub>2</sub>) among the oxidation products indicate the electrophilic or nucleophilic character of the oxidant, respectively. Both dioxides could be further oxidized to thianthrene 5,5,10-trioxide (SOSO<sub>2</sub>) (Scheme 1).

## Scheme 1. Oxidation of Thianthrene 5-Oxide with Electrophilic and Nucleophilic Oxidants



The nucleophilic parameter  $X_{Nu}$  calculated from the equation  $X_{Nu} = (SSO_2 + SOSO_2)/(SSO_2 + SOSO + 2SOSO_2)$ , i.e., nucleophilic oxidation/total oxidation, allows estimation of the nucleophilicity of the oxidant. It is widely accepted that  $X_{Nu} \leq 0.3$  is typical for electrophilic oxidants, while  $X_{Nu} \geq 0.7$  indicates nucleophilic character.<sup>61,76,78,79</sup> For UiO-66-catalyzed SSO oxidation, the value of  $X_{Nu}$  was 0.92 (Table 2), which fully

## Table 2. Oxidation of Thianthrene 5-Oxide with $H_2O_2$ over UiO-66<sup>*a*</sup>

|                             |                    | pro              | . (%) <sup>b</sup> |                   |                            |
|-----------------------------|--------------------|------------------|--------------------|-------------------|----------------------------|
| catalyst system             | SSO conversion (%) | SSO <sub>2</sub> | SOSO               | SOSO <sub>2</sub> | $\mathbf{X}_{\mathrm{Nu}}$ |
| UiO-66                      | 96                 | 88               | 0                  | 8                 | 0.92                       |
| $UiO-66 + H^{+c}$           | 62                 | 13               | 18                 | 31                | 0.47                       |
| <sup>a</sup> Reaction condi | tions: SSO 0.05 mm | а н с            | 0.05 -             | nmol Lli(         | 7 66 1                     |

"Reaction conditions: SSO 0.05 mmol,  $H_2O_2$  0.05 mmol, UiO-66 1 mg, MeCN 2 mL, 27 °C, 24 h. "Yield based on initial SSO. "Using 3  $\mu$ mol of HClO<sub>4</sub>.

agrees with a nucleophilic character of the active oxidant. The addition of  $HClO_4$  enhanced electrophilic properties of oxidant, which was manifested by decreasing the value of  $X_{Nu}$  to 0.47 (Table 2).

**Competitive Oxidation of Sulfide and Sulfoxide.** Since the use of SSO probe sometimes leads to erroneous conclusions if electron-transfer processes are involved in the oxidation process, Ballistreri et al. have suggested a complementary test for the evaluation of the oxidant electronic character, namely, competitive oxidation of sulfide and sulfoxide having different functionalities at the *p*-position under conditions when both substrates are in competition for the oxidant, which is taken in deficiency.<sup>77</sup> A considerable formation of either sulfoxide or sulfone indicates an electrophilic or nucleophilic nature of the oxidant, respectively.

The oxidation of *p*-Br-methyl phenyl sulfide and methyl phenyl sulfoxide in the presence of UiO-66 led to the preferential formation of sulfone (12%) with respect to sulfoxide (0.5%) (Scheme 2). The ratio of sulfone/sulfoxide was therefore 24, which lends further credence to the prevalence of nucleophilic oxidizing species.

## Scheme 2. Competitive Oxidation of Br-MPS and MPSO over UiO-66 $^a$



"Reaction conditions: Br-MPS 0.1 mmol, MPSO 0.1 mmol,  $H_2O_2$  0.0125 mmol, UiO-66 2 mg, MeCN 1 mL, 27 °C.

**Hammett Correlations.** To further probe the nature of the oxygen-transferring species, we evaluated the substituent electronic effect on the initial rates of sulfide and sulfoxide oxidation over UiO-66 in two series of competitive oxidation experiments carried out using *p*-substituted aryl methyl sulfides and corresponding sulfoxides (see the Experimental Section for details).

Hammett plots for the oxidation of *p*-substituted methyl phenyl sulfides displayed linear correlations (Figure 1) with negative  $\rho$  values of  $-1.0 (r = 0.979) (\sigma)$  and  $-0.74 (r = 0.990) (\sigma^+)$ , indicating an electron-demanding transition state, typical of electrophilic oxidation processes and consistent with either an

oxygen- or electron-transfer mechanism (the choice in favor of one of these two mechanisms will be made in the last section of the Results and Discussion).

However, the dependence of  $\log(k_X/k_H)$  with Hammett constants  $\sigma^{80}$  obtained for the oxidation of sulfoxides showed a linear plot with a positive slope  $\rho = +0.42$  (r = 0.998) (Figure 2), which can be considered as an unambiguous proof for domination of a nucleophilic oxidation process with a negative charge build-up on sulfur atom in the transition state. Opposite slopes in the Hammett plots acquired for the UiO-66-catalyzed sulfide and sulfoxide oxidations (Figures 1 and 2, respectively) imply a switch in the electronic character of the active oxidant from electrophilic in the first step to nucleophilic in the second one.

Collectively, all the results, including the Hammett plot, SSO probe, and competitive experiment, provide a strong experimental foundation for the formation of a reactive nucleophilic peroxo intermediate in the H<sub>2</sub>O<sub>2</sub>/Zr-MOF catalyst system. This prompted us to check whether Zr-MOFs are able to accomplish epoxidation of electron-deficient C==C bonds in  $\alpha$ , $\beta$ -unsaturated carbonyl compounds, another reaction associated with the nucleophilic type activation of hydrogen peroxide.<sup>81–84</sup>

**Epoxidation of Electron-Deficient C=C Bonds.** The catalytic performances of UiO-66 and UiO-67 were evaluated in the oxidation of two representative  $\alpha$ , $\beta$ -unsaturated ketones 2-cyclohexen-1-one and chalcone. Both Zr-MOFs revealed similar activity, showing substrate conversions considerably higher relative to blank experiments and producing corresponding epoxides with 50–60% selectivity (Table 3).

In contrast to the oxidation of S-compounds, the oxidation of less-reactive  $\alpha_{,\beta}$ -unsaturated carbonyl compounds was accompanied by oxidation of acetonitrile solvent, as evidenced by the detection of considerable amounts of acetamide in the reaction mixture. No acetamide was found in the absence of Zr-MOF or H<sub>2</sub>O<sub>2</sub>. This allowed us to assume that peroxycarboximidic acid  $H_3CC(=NH)OOH$ , the well-known intermediate formed upon the interaction of MeCN and H<sub>2</sub>O<sub>2</sub> under basic conditions, might be involved in the epoxidation of C=Cbonds over Zr-MOFs (the so-called Payne oxidation).<sup>81</sup> Acetamide can be derived from the reaction of peroxycarboximidic acid with alkene and/or hydrogen peroxide. However, the fact that the reaction readily proceeded if ethyl acetate was employed as a solvent instead of MeCN (see Table 3) suggests that a peroxo species different from peroxycarboximidic acid, e.g., a nucleophilic peroxo species derived from H<sub>2</sub>O<sub>2</sub> and Zr-MOF, may also contribute to the epoxidation of the electrondeficient C=C bonds.

**Kinetic Studies.** To gain further insight into the mechanism of the two-step thioether oxidation, reaction kinetics were investigated using both MPS and MPSO as model substrates. Typical kinetic profiles for MPS and MPSO consumption are shown in Figure 3.

Both kinetic curves show no induction period, inhibition, or autocatalytic behavior. The reaction rate was not affected by the presence of molecular oxygen and by light. Thus, any photochemical or autoxidation process can be ruled out. The comparison of the initial rates of MPS and MPSO oxidation with  $H_2O_2$  in the presence of UiO-66 (Figure 3) confirmed the significantly higher reactivity of sulfoxide:  $k_S/k_{SO} = 0.05$ .

The MPS oxidation revealed a first-order dependence of the reaction rate on the concentration of sulfide (Figure 4a). The first-order nature of the catalyst (Figure 4b) coupled with the independence of the reaction rate on the rate of stirring of the



**Figure 1.** Hammett plots for the oxidation of *p*-substituted methyl phenyl sulfides with  $H_2O_2$  in the presence of UiO-66 vs  $\sigma$  (a) and  $\sigma^+$  (b). Reaction conditions: MPS = CH<sub>3</sub>-MPS = CH<sub>3</sub>O-MPS = NO<sub>2</sub>-MPS 0.1 mmol, H<sub>2</sub>O<sub>2</sub> 0.2 mmol, UiO-66 2 mg, MeCN 1 mL, 27 °C.

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**Figure 2.** Hammett plot for the oxidation of *p*-substituted methyl phenyl sulfoxides with  $H_2O_2$  in the presence of UiO-66. Reaction conditions: MPSO =  $CH_3$ -MPSO =  $CH_3O$ -MPSO =  $NO_2$ -MPSO 0.1 mmol,  $H_2O_2$  0.1 mmol, UiO-66 2 mg, MeCN 1 mL, 27 °C.

reaction mixture suggests the lack of external diffusion limitation. As one can judge from Figure 4b, the reaction rate was not zero in the absence of catalyst, which agrees with the blank experiment provided in Table 1. The reaction order in  $H_2O_2$  was fractional (<1) and tended to decrease with increasing oxidant concentration (Figure 4c). The addition of water to the reaction mixture initially caused a reduction in the reaction rate, which then approached a constant value (after  $H_2O$ concentration reached ca. 0.4 M) (Figure 4d).

In contrast to the oxidation of MPS, the kinetics of MPSO oxidation revealed a saturation behavior for both  $H_2O_2$  and sulfoxide reactants (Figure 5a,c). The negative effect of water on the reaction rate (Figure 5d) can be rationalized if we suggest that  $H_2O$  adsorbs on the catalyst surface and competes with the reactants for the active Zr sites. Subsequent adsorption studies and kinetic modeling of MPSO oxidation fully confirmed this hypothesis.

Arrhenius activation energies measured for MPS and MPSO oxidation over UiO-66 were found to be similar (40 and 38 kJ/ mol, respectively; Figure 6). Such a value of the activation parameter is quite typical of homogeneous thioether oxidations<sup>85,86</sup> and implies that the reaction rate is controlled by chemical interaction rather than diffusion of reactants (in the latter case, one might anticipate  $E_a < 20-30$  kJ/mol).<sup>87</sup>

Adsorption Studies. Investigation of the liquid-phase adsorption of S-compounds showed that adsorption of MPS and MPSO<sub>2</sub> on UiO-66 from MeCN is minor if not zero (Figure

S9), while adsorption of MPSO is notable (Figure 7). In contrast, adsorption of sulfoxide from a MeCN $-H_2O$  mixture, where water concentration was close to the concentration of water (including that derived from hydrogen peroxide) in a typical MPSO oxidation experiment, was much lower relative to adsorption from pure MeCN (compare adsorption isotherms in Figure 7). This unambiguously indicates that concurrent adsorption of water and MPSO takes place on the UiO-66 surface.

Kinetic Modeling of MPSO Oxidation. Overall, a general mechanism of sulfoxide oxidation can be tentatively described by eqs 1-5, which reflect possible ligand exchange in the coordination sphere of Zr(IV) and intramolecular oxygen transfer from a peroxo zirconium species to sulfoxide ligated to another Zr(IV) site:

$$\begin{array}{c} H_2O \\ \downarrow \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ \downarrow \\ Zr \\ OH \end{array} + H_2O_2 \xrightarrow{K_2} \downarrow \\ Zr \\ OH \end{array} \begin{array}{c} H_2O_2 \\ \downarrow \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ \downarrow \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ \downarrow \\ Zr \\ OH \end{array}$$
 (2)

$$\begin{array}{c} H_2 O \\ I \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ I \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ I \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ I \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ I \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ I \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ I \\ Zr \\ OH \end{array} \begin{array}{c} R_2 \\ I \\ Zr \\ OH \end{array}$$

$$\begin{array}{cccc} \text{MPSO} & \text{OOH} & \text{MPSO}_2 & \text{OH} \\ & & & \\ \text{Zr} & & & \\ \text{OH} & \text{Zr} & & \\ \text{OH} & \text{Zr} & & \\ \end{array} \xrightarrow{} & \text{Zr} & \begin{array}{c} \text{OH} & \\ \text{OH} & \text{Zr} & \\ \text{OH} & \\ \end{array}$$
(5)

 $R_1 = H_2O, H_2O_2, MPSO, MPSO_2$   $R_2 = OH, \eta^2-OO$ 

Note that peroxide formation implies also the formation of H<sup>+</sup>. For simplicity, we placed this proton on the peroxo group (eq 1), but other possible sites of its location will be discussed in the following sections. The set of eqs 1–5 was used to build a kinetic model of MPSO oxidation (see the Supporting Information for details). On the basis of the results of the adsorption study, equilibrium constant  $K_4$  was intentionally assumed to be low (<10<sup>-3</sup>). All parameters of the model are provided in Table S2.

Figure S10 demonstrates that experimental kinetic curves are quite well described by the proposed kinetic scheme. We note

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| Substrate | Solvent            | Catalyst | Time | Substrate | Product | Epoxide         |
|-----------|--------------------|----------|------|-----------|---------|-----------------|
|           |                    |          | (h)  | conv. (%) |         | select. (%)     |
|           | CH <sub>3</sub> CN | UiO-66   | 1    | 20        | 0       | 60 <sup>b</sup> |
|           | EtOAc              | UiO-66   | 2    | 18        |         | 45              |
|           | CH <sub>3</sub> CN | UiO-67   | 1    | 20        |         | 55              |
|           | EtOAc              | UiO-67   | 2    | 20        |         | 55              |
|           | CH <sub>3</sub> CN | _        | 1    | 5         |         | c               |
|           | CH <sub>3</sub> CN | UiO-66   | 0.5  | 30        |         | 50 <sup>d</sup> |
|           | CH <sub>3</sub> CN | UiO-67   | 0.5  | 40        |         | 40              |
|           | CH <sub>3</sub> CN | _        | 2    | 5         |         | e               |

<sup>*a*</sup>Reaction conditions: substrate 0.1 mmol,  $H_2O_2$  0.8 mmol, UiO-66 or UiO-67 5.0 mg, MeCN 1 mL, 70 °C. <sup>*b*</sup>Other products: 4-acetylbutyric acid, 3-hydroxycyclohexanone, 4-hydroxy-2-cyclohexen-1-one. <sup>*c*</sup>Trace amounts of epoxide. <sup>*d*</sup>Other products: benzaldehyde, benzoic acid, and dibenzoylmethane. <sup>*e*</sup>Main products were benzaldehyde and benzoic acid; no epoxide was found.



**Figure 3.** Kinetic profiles of MPS and MPSO oxidation with  $H_2O_2$  in the presence of UiO-66. Reaction conditions: MPS or MPSO 0.125 mmol,  $H_2O_2$  0.125 mmol, UiO-66 1 mg, MeCN 5 mL, 27 °C.

that the value of the equilibrium constant  $K_3$  of the MPSO-H<sub>2</sub>O exchange on the Zr site obtained from the kinetic data (Table S2) assumes that MPSO possesses a greater affinity to the UiO-66 surface than H<sub>2</sub>O does. However, if the concentration of water is rather high, then the adsorption of sulfoxide is expected to be suppressed, which is consistent with the experimental observations (Figure 7).

Some other trends in the MPS oxidation kinetics could also be explained on the basis of the kinetic modeling of MPSO oxidation. Keeping in mind that the sulfide oxidation is much slower than the oxidation of sulfoxide and that the rate of the formation of active peroxo species is comparable with the rate of MPSO oxidation (see Table S2 and corresponding comments in the Supporting Information), MPS oxidation to MPSO may be considered a rate-limiting stage of the overall oxidation process. This agrees with the nearly linear dependence of the MPS oxidation rate on MPS concentration (Figure 4a).

**Raman Spectroscopic Study.** Raman spectroscopy was employed to probe the interaction of Zr-MOF with aqueous hydrogen peroxide in MeCN medium. Figure 8 shows changes in the Raman spectrum of UiO-66 after various treatments with  $H_2O_2$ .

We did not observe a characteristic peak from a physisorbed  $H_2O_2$ , which is usually manifested at 867–875 cm<sup>-1</sup>,<sup>88–90</sup> probably because of its low intensity and/or overlapping with the vibrations of Zr-MOF itself. However, we did note the appearance of two new Raman features, at 834 and 1124 cm<sup>-1</sup>, associated with the reaction of Zr(IV) with  $H_2O_2$ . According to



**Figure 4.** Initial reaction rates of MPS oxidation vs concentration of (a) MPS, (b) UiO-66, (c)  $H_2O_2$ , and (d)  $H_2O$ . Reaction conditions: MeCN 5 mL, 27 °C; (a) UiO-66 1 mg,  $H_2O_2$  0.025 M,  $H_2O$  0.09 M; (b) MPS 0.025 M,  $H_2O_2$  0.025 M,  $H_2O$  0.09 M; (c) MPS 0.025 M, UiO-66 1 mg,  $H_2O$  0.36 M; (d) MPS 0.025 M,  $H_2O_2$  0.025 M, UiO-66 1 mg.

the literature, the band at  $834 \text{ cm}^{-1}$  can be assigned to the O–O stretching mode of a peroxide ligand, which is usually observed in the range of  $820-860 \text{ cm}^{-1}$  in the vibrational spectra of zirconium peroxo complexes.<sup>75,91–95</sup> The intensity of this band markedly increased if the sample was not washed with MeCN after the treatment (spectrum D in Figure 8). However, at a high residual concentration of H<sub>2</sub>O<sub>2</sub>, some other additional bands also arose in the spectrum, probably indicating the beginning of MOF degradation (spectrum D in Figure 8). Importantly, the excess of the oxidant in the catalytic experiments was lower than in the Raman study (see the Experimental Section), ensuring the stability of the catalyst under turnover conditions.

A comparison of the Raman spectra of  $H_2O_2$ -treated UiO-66 and  $(Zr_6)_2$  cluster collected under similar conditions (Figure S11) shows that the position of the new band assigned to O–O stretching vibrations in the spectrum of Zr-MOF (834 cm<sup>-1</sup>) is close to the one arising in the spectrum of the  $(Zr_6)_2$  cluster (842 cm<sup>-1</sup>). Note that the growing intensity of this band is accompanied by the loss of the cluster structure, which is fully consistent with the results reported earlier by Carraro and coworkers.<sup>75</sup>

The second intensive band that appears in the Raman spectrum at 1124 cm<sup>-1</sup> after interaction of UiO-66 with  $H_2O_2$  most likely indicates the generation of a superoxide complex (typical O–O stretching vibrations 1050–1200 cm<sup>-1</sup>).<sup>91,96,97</sup> This is not surprising if we remember that UiO-66 possesses significant activity in  $H_2O_2$  decomposition in the absence of organic substrate.<sup>41</sup> This band is absent in the spectrum of  $H_2O_2$ -treated (Zr<sub>6</sub>)<sub>2</sub>, which may correlate with its lower activity in  $H_2O_2$  degradation.

FTIR Study of Surface Acid–Base Properties of UiO-66. As was mentioned in the Introduction, the presence of both Lewis and Brønsted acid sites (LAS and BAS) is crucial for catalytic performance of UiO-66. This prompted us to probe LAS and BAS in the UiO-66 catalyst using FTIR spectroscopy of a weakly interacting base, CO (see the Supporting Information for details). Upon CO adsorption, the band of isolated hydroxyl groups shifted from 3674 cm<sup>-1</sup> to the low-frequency region (Figures S12 and S13). The absolute value of this shift was 75 cm<sup>-1</sup>, which lies within the range of the previously reported values of 69-83 cm<sup>-1</sup>.<sup>98-100</sup> An estimation of the strength of the BAS in the proton affinity scale (eq S1) gave the value of 1425 kJ/mol, which characterizes the acidity of these OH groups as very weak.

FTIR spectra of adsorbed CO in the carbonyl region (Figure S14) revealed the presence of strong bands at 2152 and 2135 cm<sup>-1</sup> attributed to CO adsorbed on OH groups and physically adsorbed CO, respectively, and a weak shoulder in the range of 2170-2180 cm<sup>-1</sup>, which can be related to a minor amount of LAS.<sup>98,101</sup> In contrast to the previous studies, <sup>98,101</sup> this band could not be observed at low CO pressures (Figure S14), which may be considered an indication of the absence of a significant amount of defects and undercoordinated Zr(IV) sites in the hydroxylated UiO-66 sample used in this work.

In addition, adsorption of  $\text{CDCl}_3$  was used to estimate the amount and strength of basic sites present in the UiO-66 catalyst. This method has been widely employed for exploring basic sites in various heterogeneous catalysts.<sup>84,102–108</sup> The IR spectra of  $\text{CDCl}_3$  after adsorption on the UiO-66 sample are presented in Figure 9.

Two bands at 2252 and 2268 cm<sup>-1</sup> can be disclosed after the deconvolution of the absorption band at 2200–2300 cm<sup>-1</sup>. According to the literature, the absorption at 2252 cm<sup>-1</sup> can be assigned to C–D stretching vibration of CDCl<sub>3</sub> molecules



**Figure 5.** Initial reaction rates of MPSO oxidation vs concentration of (a) MPSO, (b) UiO-66, (c)  $H_2O_2$ , and (d)  $H_2O$ . Reaction conditions: MeCN 5 mL, 0 °C; (a) UiO-66 1 mg,  $H_2O_2$  0.025 M,  $H_2O$  0.09 M; (b) MPSO 0.025 M,  $H_2O_2$  0.025 M,  $H_2O$  0.09 M; (c) MPSO 0.025 M, UiO-66 1 mg,  $H_2O$  0.36 M; (d) MPSO 0.025 M,  $H_2O_2$  0.025 M,  $H_2O_2$ 



**Figure 6.** Arrhenius plots for MPS (red  $\bullet$ ) and MPSO (black  $\blacksquare$ ) oxidation with H<sub>2</sub>O<sub>2</sub> in the presence of UiO-66. Reaction conditions: MPS or MPSO 0.025 M, H<sub>2</sub>O<sub>2</sub> 0.025 M, UiO-66 1 mg (MPS) or 2 mg (MPSO), MeCN 5 mL.

hydrogen-bonded to basic sites, while the 2268 cm<sup>-1</sup> feature corresponds to CDCl<sub>3</sub> in the gas phase.<sup>102,103,108</sup> The strength of basic sites in terms of proton affinity calculated using eq S2 was 843 kJ/mol and characterized them as weak basic sites. A similar value of PA (839 kJ/mol) was reported for UiO-66 prepared using a different methodology.<sup>108</sup> The number of basic sites roughly assessed from the integral intensity of the band at 2252 cm<sup>-1</sup> was ca. 230  $\mu$ mol/g.

**Evaluation of Basicity by Adsorption of Isobutyric Acid.** Given that quantification of acid and basic sites from IR data of probe molecules can be imprecise because of uncertainty in the molar extinction coefficient, which may depend on both the particular adsorbate and adsorbent, <sup>107,109</sup> we also attempted



**Figure 7.** Adsorption isotherms of MPSO from MeCN (black  $\blacksquare$ ) and MeCN-H<sub>2</sub>O (red  $\bullet$ ) (0.125 M H<sub>2</sub>O) on UiO-66 at room temperature.

to evaluate the number of basic sites in the Zr-MOFs by adsorption of isobutyric acid (IBA) from *n*-hexane using an approach similar to that recently employed for the determination of the intrinsic basicity of Nb-containing hydroxyapatites.<sup>50</sup> Figure 10 shows adsorption isotherms for the fresh UiO-66 sample and the sample preliminary saturated with IBA and then washed with the solvent (see the Supporting Information for details). We note that strong, irreversible adsorption of IBA occurs only on the fresh sample. Insignificant adsorption observed for the IBA-saturated sample may be related to week physical adsorption of the acid.

Two types of potential basic sites have been suggested in the literature for UiO-66:  $\mu^3$ -oxygens bridging Zr-atoms<sup>34</sup> and terminal hydroxyls of ZrOH created in the MOF defects.<sup>27,35,110,111</sup> Nowadays, it is widely accepted that one missing linker in Zr-MOF is replaced with two couples of  $-OH_2$ 



**Figure 8.** Raman spectra of fresh UiO-66 (A) and  $H_2O_2$ -treated UiO-66: (B and C) 30- and 90-fold excess of  $H_2O_2$  followed by washing with MeCN; (D) 60-fold excess of  $H_2O_2$  without washing.



**Figure 9.** FTIR difference spectra of CDCl<sub>3</sub> adsorbed on UiO-66 sample. Deconvolution curves are shown as dotted lines.



**Figure 10.** Adsorption of IBA on UiO-66 (fresh, red  $\bullet$ ; IBA-saturated, black  $\blacksquare$ ) from *n*-hexane at 25 °C.

and -OH groups to compensate for the charge lost.<sup>27,35,110–112</sup> The most common representation of the defect open site is depicted in Figure 11 (structure A). In addition, two complementary structures (B and C) were also proposed.<sup>112–114</sup>

Recent DFT studies implicated that basic sites in hydrated UiO-66 are, most likely, the terminal ZrOH groups.<sup>27,35</sup> However, these groups were also considered very weak acidic sites,<sup>11,115</sup> which is not surprising given that an amphoteric character of zirconium hydroxide is well-known.<sup>116</sup> Using molecular dynamics simulations, Ling and Slater revealed the existence of a dynamic acidity at defect sites of UiO-66, alternating between hydroxide and water.<sup>111</sup>



Article

**Figure 11.** Simplified representation of open sites formed in defects of Zr-MOF.

The amount of ZrOH groups in the structure of defective UiO-66 with 10.8 BDC linkers calculated on the basis of the formula  $Zr_6O_4(OH)_4(C_8H_4O_4)_{5.4}[(H_2O)(OH)]_{1.2}$  is 740  $\mu$ mol/g. The concentration of basic sites in UiO-66 estimated from the IBA adsorption isotherm (Figure 10) was ca. 700  $\mu$ mol/g. This value is higher than the one assessed by the IR spectroscopic technique with CDCl<sub>3</sub> probe molecule (ca. 230  $\mu$ mol/g), but it seems to be in a good agreement with the calculated concentration of basic sites (700 vs 740  $\mu$ mol/g). A rather good match was also observed for UiO-67 (1300 vs 1150  $\mu$ mol/g calculated for MOF with two missing linkers; Figure S17). Therefore, we have fairly good accordance between the estimation of missing-linker defects by TGA and the evaluation of basic sites by adsorption of IBA. Further studies will show how applicable this approach could be to other MOF materials.

**Presumable Active Species and Proposed Oxidation Mechanism.** Several conceivable structures of peroxo zirconium species that might be responsible for the nucleophilic oxygen transfer in Zr-MOF-catalyzed oxidations are presented in Figure 12. Taking into account experience in the chemistry of metal-oxo clusters or polyoxometalates (POMs) comprising a  $M_2(\mu$ -OH)<sub>2</sub> or  $M_2(\mu$ -O)( $\mu$ -OH) core (M = Ti, Zr, and V),<sup>90,117-120</sup> we may cautiously assume the existence of both terminal and bridging peroxo intermediates for Zr-MOF either. Indeed, free energy barriers computed for the H<sub>2</sub>O<sub>2</sub> activation by Ti–OH and Ti<sub>2</sub>( $\mu$ -OH) moieties in [( $\gamma$ -SiTi<sub>2</sub>W<sub>10</sub>O<sub>38</sub>H<sub>2</sub>)-(OH)<sub>2</sub>]<sup>4-</sup> turned out to be almost isoenergetic, 21.2 and 21.3 kcal mol<sup>-1</sup>, respectively.<sup>119</sup> It was also demonstrated that acidic Zr–(OH)–Zr group in POMs is able to react with aqueous H<sub>2</sub>O<sub>2</sub><sup>90</sup> or methanol.<sup>118</sup> However, we should remember that reactivity of  $\mu$ <sup>3</sup>-OH groups in Zr-MOFs is expected to be lower than reactivity of  $\mu$ <sup>2</sup>-OH bridges in POMs.

Structures II and III reflect the transformation of electrophilic zirconium hydroperoxo species into nucleophilic ones through hydrogen bonding of the proton to basic site, similar to what was suggested by Neumann and co-workers for a Bi-substituted POM.<sup>73</sup> Other structures depicted in Figure 12 might be derived from these two key structures. Zirconium peroxo complexes with a mono- (structure VI) or bis- $\mu$ - $\eta^2$ : $\eta^2$  arrangement of the peroxo ligand have been documented in the literature,<sup>95</sup> while structures similar to structure IV were suggested for a range of nucleophilic oxidations.<sup>60,62</sup>

In contrast to terminal peroxo intermediate I, no expansion of the Zr(IV) coordination sphere would occur for the other structures, which might be more reasonable from the energetic point of view. Indeed, DFT calculations of Limvorapitux et al. discarded structure I as energetically not feasible.<sup>39</sup> Nevertheless, at the moment, we cannot completely rule out the participation of the terminal peroxo species in the oxidation of sulfoxide. Theoretical studies of Hajeck et al. implicated that hydrated bricks in UiO-66 have rather strong basic sites ( $\mu^3$ oxygen atoms) which facilitate protonation steps.<sup>34</sup> Moreover, we cannot exclude that a partial (maybe, reversible) cleavage of an additional Zr–BDC junction may occur, either to release



Figure 12. Conceivable structures of nucleophilic peroxo zirconium species.





<sup>*a*</sup>Terminal option: A, bridging option: B.

strain around the Zr center in structure I or the like, similar to what has been recently suggested for a hydroperoxo titanium species formed in a sterically hindered environment.<sup>121</sup> We hope that further computational studies would shed light on this matter.

Finally, we would like to discuss the mechanism of the first step of the thioether oxidation process, that is, the formation of intermediate sulfoxide. The use of Hammett parameter  $\sigma^+$ (Figure 1b) gave better correlation (r = 0.997) than that of  $\sigma$ (Figure 1a), which is sometimes considered as a manifestation of a single electron transfer mechanism (SET) that involves the formation of an intermediate thioether radical cation followed by its rapid capture by water and further oxidation.<sup>122</sup> However, oxidation of MPS with  $H_2O_2$  in the presence of labeled water  $H_2^{18}O$  (98% enriched) revealed no isotopic incorporation in the sulfoxide and sulfone products, which implies that the vast majority of oxygen in the products arises from hydrogen peroxide and not from water. The choice in favor of the electrophilic oxygen transfer mechanism at the first stage of the thioether oxidation process was further supported by the product analysis in the oxidation of the well-known test substrate benzyl phenyl sulfide (BPS). The corresponding sulfone was the principal oxidation product (ca. 90% selectivity), while the amount of products that might be derived from radical cation fragmentation and/or dimerization (benzaldehyde, benzoic acid, and dibenzyl)<sup>123,124</sup> was minor even in comparison with the reaction in the presence of the well-known oxygen-transfer agent, the Venturello complex  $(THA)_3[PO_4\{WO(O_2)_2\}_4]$  (see Figure S15). Finally, oxidation of diethyl sulfide was ca. 3 times faster than oxidation of MPS (Figure S16), which argues against SET mechanism, for which the opposite trend would be anticipated.<sup>57</sup> All the data strongly support electrophilic oxygen transfer mechanism at the first stage of the thioether oxidation over Zr-MOF leading to sulfoxide, which is immediately oxidized further to sulfone via nucleophilic oxygen transfer mechanism. Deceleration of the UiO-66-catalyzed thioether oxidation by acid additives (see Table 1) agrees with this hypothesis. Indeed, one might predict that protonation of thioether would decrease its nucleophilicity and thereby hamper its interaction with an electrophilic oxidant.

Taking into account the switch in the philicity of the oxygen atom transfer in the oxidation of thioethers and sulfoxides over Zr-MOF, we suggest either a biphilic nature of the active peroxo intermediate or the existence of an equilibrium between the two types of peroxo zirconium species, which might be responsible for nucleophilic and electrophilic oxygen transfer to sulfoxide and sulfide, respectively. The positive effect of protons on the sulfoxide selectivity observed in this work inclined us to the second assumption. Indeed, in the presence of acid additives, the yield of sulfoxide increased (Table 1) while nucleophilic parameter  $X_{Nu}$  in the oxidation of thianthrene 5-oxide decreased (Table 2). "Terminal" and "bridging" versions of possible equilibriums are shown in Scheme 3A,B, respectively. These equilibriums would shift right or left, depending on the surface and medium acidity.

Overall, we tentatively propose the mechanism of the oxidation of S-compounds in nonprotic solvents where slow bimolecular oxidation of thioether by electrophilic Zr hydroperoxo species is followed by fast intramolecular oxidation of sulfoxide with nucleophilic Zr peroxo intermediate (Scheme 4). The presence of basic sites in Zr-MOF favors the generation of

Scheme 4. Proposed Catalytic Cycle of Thioether Oxidation over Zr-MOF



nucleophilic oxidant which, coupled with chemisorption of intermediate sulfoxide, results in the superior yield of sulfone. Although structure III was selected to draw Scheme 4, the alternative nucleophilic species depicted in Figure 12 might also participate in the proposed catalytic cycle.

Previously, Limvorapitux et al. rationalized the augmented sulfoxidation selectivity in MeOH in terms of a competition between the solvent and sulfoxide for the UiO-66 open sites.<sup>39</sup> This suggestion seems to be reasonable; however, another reason might be ligation of methanol to the active site, leading to a  $\eta^1$ -hydroperoxo intermediate with enhancing electrophilic properties, or hydrogen-bonding with nucleophilic oxygen of the peroxo species, resulting in its partial deactivation. Recent theoretical studies on UiO-66 showed that methanol assists in the proton mobility through a hydrogen-bonded network.<sup>35</sup>

#### CONCLUSIONS

In this work, we systematically investigated the mechanism of the two-step sulfide-sulfoxide-sulfone oxidation with aqueous hydrogen peroxide over Zr-MOF, in particular UiO-66, by analyzing the oxidation products and reactivity of various test substrates as well as by using kinetic, adsorption, and spectroscopic tools. Hammett correlations revealed an unambiguous proof of a switch in the philicity of the active oxidant from electrophilic in the first step to nucleophilic in the second step. All the results collectively allowed us to suggest that  $H_2O_2$ is activated on Zr(IV) sites to produce a hydroperoxo zirconium species, "ZrOOH", possessing electrophilic properties, but an adjacent basic oxygen atom implements deprotonation (maybe, partial) of "ZrOOH", thereby favoring its transformation into a nucleophilic oxidant. While "ZrOOH" ensures the first step of the thioether oxidation, its nucleophilic counterpart fulfills oxygen transfer to S atom of sulfoxide. The nucleophilic peroxo intermediate is also capable to epoxidize electron-deficient C= C bonds in  $\alpha_{\beta}$ -unsaturated carbonyl compounds. The unprecedentedly high selectivity toward sulfones observed with an equimolar amount of H<sub>2</sub>O<sub>2</sub> implies that nucleophilic activation of hydrogen peroxide predominates over electrophilic one in Zr-MOFs. Acid additives increase sulfoxidation selectivity, suggesting that protons assist in the transformation of the nucleophilic peroxo zirconium intermediate to the electrophilic hydroperoxo one. We hope that further theoretical studies may elucidate the structure of the active peroxo species and the mechanism of their formation.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01084.

Full details on the Zr-MOF synthesis and characterization, spectroscopic and adsorption measurements, and kinetic modeling (PDF)

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#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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