

# Modified Metal-Organic Frameworks - Synthesis, Properties and Potential in Catalysis

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**Peroxynitrate Formation During Peroxynitrite Decomposition**

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Peroxynitrous acid is an unstable peracid which is known to isomerize in a first-order reaction to nitrate with a rate constant of  $1.2 \text{ s}^{-1}$ . A kinetic anomaly was observed together with dioxygen and nitrite formation at  $\text{pH} = 7-8$ , just above the  $\text{pK}_a$  [1]. Since other peracids do undergo bimolecular decomposition regularly [2], we suspected that such a reaction could compete with the unique isomerization. An intermediate was never characterized for the other peracids, it is thought to be too short-lived [3].

We were able to detect the electronic spectrum of peroxynitrate during peroxynitrite decomposition with a quenching method. The peroxynitrate quantities formed were determined by conversion of iodide to iodine after complete elimination of peroxynitrite. The relative yields depend on initial peroxynitrite concentration, as expected for a bimolecular process competing with a monomolecular one. The absolute peroxynitrate yields were more than two times higher than expected from the radical decomposition mechanisms favored by many biochemists [4], providing the second confirmation of a bimolecular interaction. Finally, we could satisfactorily simulate the kinetic anomalies observed earlier.

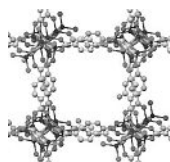
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**Modified Metal-Organic Frameworks – Synthesis, Properties and Potential in Catalysis**

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Due to their microporous structure, metal-organic frameworks have become an interesting and promising class of materials for applications in heterogeneous catalysis.<sup>[1]</sup> Based on MOF-5 and the corresponding IRMOF series<sup>[2]</sup>, we present new methodologies for the modification of metal-organic frameworks with functional groups and active metal centers.



In general, such modification of MOFs with catalytically active groups strongly influences the physical and chemical properties. Therefore special attention is given to the characterization of the resulting catalyst materials under catalytic conditions.

The studies include investigations on the thermal stability of such materials under inert and oxidizing atmosphere as well as the stability in common solvents and supercritical  $\text{CO}_2$ . Based on these results, we were able to disclose the scope and limitations of our materials for possible catalytic applications. The modified materials could be utilized in gas-phase oxidation reactions as well as in catalytic processes in supercritical  $\text{CO}_2$ .

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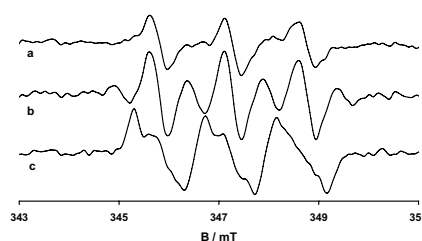
**NO autoxidation in aqueous solution studied by electron spin resonance spectroscopy**

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The mechanism of  $\text{NO}^\bullet$  autoxidation has been proposed via nitric oxide dimer  $(\text{NO})_2$  or nitrosyldioxy radical  $(\text{ONOO}^\bullet)$ . We found evidence for  $\text{ONOO}^\bullet$  being the intermediate in the gas phase by ESR spectroscopy.

Based on the gas phase result, we estimated the steady-state concentration of  $\text{ONOO}^\bullet$  to be around  $10^{-14} \text{ M}$  for the autoxidation in aqueous solution, of which the overall rate is also well-known. We show that a spin trap forms different products if treated with a fresh  $\text{NO}^\bullet/\text{air}$  mixture compared to the action of the final autoxidation product,  $\text{NO}_2^\bullet$ . The reaction product with  $\text{NO}_2^\bullet$  in aqueous solution does not correspond to the one obtained in benzene [1]. Further, we present results of the direct EPR detection attempt on  $\text{ONOO}^\bullet$ .



EPR spectra of 20 mM 5,5-Dimethylpyrroline-N-oxide exposed for 1 h to  $\text{NO}^\bullet/\text{air}$  (a), air (b) and  $\text{NO}_2^\bullet/\text{air}$  (c). 100 mM acetate buffer,  $\text{pH} = 5$ .

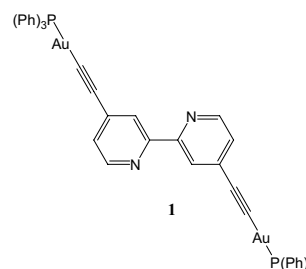
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**Gold(I) phosphine derivatives of 4,4'-dialkynyl substituted 2,2'-bipyridine**

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Gold(I) phosphine derivatives have the potential to be luminescent and have interesting optical properties [1]. Ligand **1** can be synthesized from 4,4'-dialkynyl substituted 2,2'-bipyridine and triphenylphosphine gold(I) chloride. This compound had been structurally characterized, and related compounds will also be described and their absorption and emissive properties discussed. We plan to complex this ligand with transition metals like ruthenium(II) and iron(II) in order to investigate the effects of coordination on their electronic spectroscopic properties.



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