LOW TEMPERATURE MASS SPECTROMETRY AS A POTENT TOOL FOR STUDYING REACTION MECHANISMS

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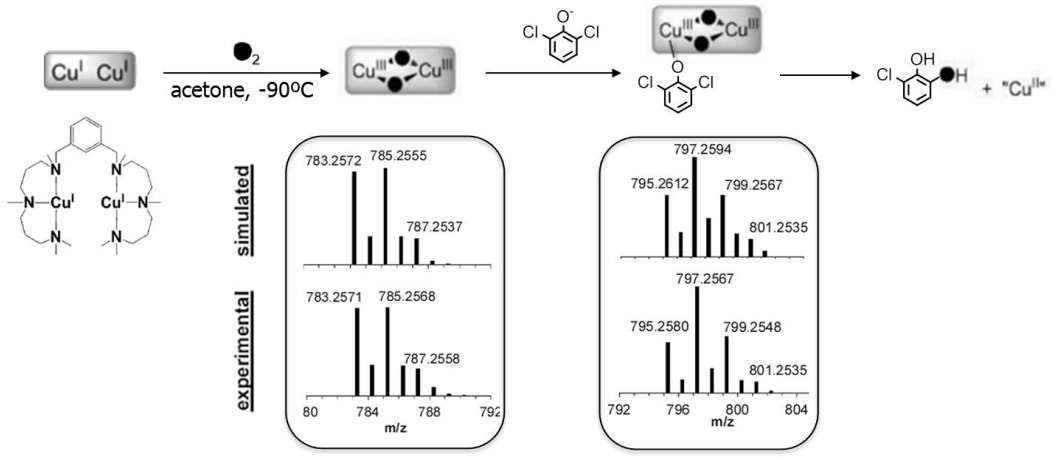
The isolation and characterization of intermediates is a key step for the understanding of reaction mechanisms and the design of more efficient catalysts. Unfortunately, this is usually hampered by the short life time and thermolability of such species. Mass spectrometry is a useful tool for characterization since it allows detecting minor species of a mixture, which is particularly useful in the case of the detection of intermediate species. However, high temperatures (150ºC) are typical ionization conditions, even in the soft ESI ionization, hampering its application in the characterization of intermediate species. To address this problem herein we present the combination of a Cryospray attachment with a high resolution mass spectrometer (HRMS) for the characterization of very unstable intermediate species. This approach allowed us, for example, to monitor the reaction of a dimeric Cu(I) complex with oxygen in acetone at -90ºC. Further reaction of the bis-μ-oxo Cu(III) complex with phenolates showed the presence of an association complex. This intermediate was previously detected by UV-Vis but its formulation remained unclear until we studied it by low temperature mass spectrometry.[1] Furthermore, Cryo-HRMS was also used to characterize iron-oxo intermediates in water or acetonitrile showing the broad scope of this approach in the study of mechanisms.[2,3]



CRYO-HRMS: Nebulizer and dry gas set at: -90ºC

1) J. Serrano-Plana, I. Garcia-Bosch, R. Miyake, M. Costas, A. Company. *Angew. Chem. Int. Ed.*, **2014**, 53(36), 9608.
2) Z. Codolà, L. Gómez, S. T. Kleespies, L. Que Jr., M. Costas, J. Lloret-Fillol, *Nature communications*; **2015**, *6*, 5865.
3) O. Planas, M. Clémancev, J-M. Latour, A. Company, M. Costas. *Chem. Commun.*, **2014,** 50**,** 10887.