

Review

The application of electrospray ionization mass spectrometry to homogeneous catalysis



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ABSTRACT

Electrospray ionization mass spectrometry (ESI-MS) is increasingly being used as a tool to gain mechanistic insights into homogeneous metal-catalyzed reactions. Here we briefly discuss the advantages of ESI-MS for studying solution-phase reactions and review the work that has been conducted in the area to date. In order to investigate any catalytic system by ESI-MS all species of interest must be charged: either inherently, adventitiously or intentionally by installing a charged or chargeable tag. This review will be organized accordingly. In addition, a portion of the review is devoted to the emerging use of ESI-MS to collect continuous kinetic data on reactants, products and reactive intermediates by in situ, real-time analysis of catalytic reaction mixtures. The review covers work in the field up to 2013.

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1. Introduction

Metal-catalyzed reactions are a proven and powerful tool in the endeavour to address future energy needs and to develop modern materials. However, in order to fully capitalize on the potential benefits of these types of reactions more detailed information is required on the workings of metal catalysts under their normal operating conditions. Electrospray ionization mass spectrometry (ESI-MS) can provide access to mechanistic information that is difficult or even impossible to attain using standard spectroscopic techniques. There are a number of things that make mass spectrometry, and especially ESI-MS, well suited to the study of products, reactants and catalytic intermediates in metal-catalyzed reactions: ESI-MS is a soft technique that operates on solutions and can leave weak bonding interactions intact; only species that are already

charged in solution or contain an easily charged site are detected, so most common solvents are “invisible” and very low detection limits are accessible [1,2]; analysis is fast (on the order of seconds), and intermediates at nanomolar concentrations can be detected with ease; finally, since each species in solution is usually represented by a single peak in the mass spectrum, it is relatively simple to extract information from complex mixtures.

A growing body of literature exists in which investigators have taken advantage of these attributes of ESI-MS to study organometallic systems. The first was Berman who used ESI-MS to detect a number of environmentally important organoarsenic ions [3]. Another notable early example comes from Canty in 1993 who reported the positive ESI-MS and tandem MS studies of various palladium and platinum organometallic complexes [4]. Since then, the primary use of ESI-MS in the area of solution-phase organometallic chemistry has been in the identification of short-lived, low concentration intermediates from catalytic mixtures. Towards this end, ESI-MS has been used to study catalytic oxidations [5–8], hydrogenations [9–11], hydrosilylations

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[12] and carbon-carbon bond-forming [13–15] reactions with the most attention given to palladium-catalyzed carbon-carbon bond-forming reactions [14,16–21]. A number of book chapters have been written on the subject of ESI-MS analysis of organometallic reaction intermediates [22–24] and this review aims to highlight more recent advances and new directions in the field.

It is important to mention that a range of mass spectrometry techniques also exist which allow organometallic ions of interest to be isolated and studied directly in the gas phase. These methods contribute significantly to the utility of mass spectrometry as a mechanistic tool in organometallic chemistry, but this review will focus solely on reactions occurring in homogeneous solutions. For an overview of gas-phase studies of organometallic complexes see the excellent reviews by Traeger [25], Plattner [26], Holčapek [27] and Schröder [28]. New advances in the field of ion spectroscopy deserve mention; namely, the detailed structural characterization of reactive intermediates within a mass spectrometer [29].

In order to investigate any catalytic system by ESI-MS all species of interest must be charged; either inherently, adventitiously (e.g. by protonation or loss of a halide) or intentionally by installing a charged or chargeable tag: the studies discussed will be organized accordingly. It is worth noting that although most investigations to date have focused on palladium or ruthenium systems there is no inherent limitation to which metals can be investigated by ESI-MS as long as the species are charged. The final part of this review is devoted to the emerging use of ESI-MS to collect continuous real-time kinetic data on catalytic transformations including direct kinetic analysis of individual elementary reaction steps.

2. Inherently-charged systems

Reactions with inherently charged intermediates allow for straightforward analysis – the standard reaction mixture can simply be sampled and infused directly into the mass spectrometer. Oxidation reactions lend themselves particularly well to this method of analysis since the reaction intermediates are often inherently charged. A range of manganese-containing intermediates for a variety of reactions have been observed and the groups of Bortolini [30,5,31,32] and Smith [33,7,34] have been strong contributors to research in this area.

Among the first reports was the investigation of an iron-catalyzed oxidation system in 1997. ESI-MS was used to characterize the intermediate $[\text{Fe}^{\text{III}}\text{-TPA}(\text{OOH})]^{2+}$ in the stereospecific hydroxylation of alkanes by hydrogen peroxide (TPA, tris(2-pyridyl-methyl)amine) [35]. It is unique among oxidation reactions studied by ESI-MS in that all other reports address manganese- or vanadium-catalyzed systems.

In 1998 evidence for the existence of a commonly invoked intermediate for a variety of oxygen transfer reactions involving the $[\text{O}=\text{Mn}^{\text{V}}]$ moiety was obtained by interception of an $[\text{O}=\text{Mn}^{\text{V}}(\text{salen})(\text{OIPh})]^{+}$ complex (Fig. 1A) and a binuclear $[\mu\text{-O}(\text{Mn}^{\text{IV}}(\text{salen})(\text{OIPh}))_2]^{2+}$ complex (Fig. 1B) [36]. Later, an ESI-MS study on the Mn-catalyzed oxidative kinetic resolution of secondary alcohols by $\text{PhI}(\text{OAc})_2$ reported the observation of a similar manganese salen intermediate $[\text{Mn}^{\text{V}}(\text{salen})(\text{PhIO})(\text{OCH}(\text{CH}_3)\text{Ph})]^{+}$ (Fig. 1C) [6]. This, along with the observation of $[\text{Mn}^{\text{III}}(\text{salen})(\text{PhI}(\text{OAc})_2)]^{+}$ (Fig. 1D), allowed the proposal of a possible catalytic cycle for the kinetic resolution of secondary alcohols by this system.

Mn-MeTACN complexes have been studied extensively by ESI-MS in the oxidation of a variety of organic substrates using hydrogen peroxide (MeTACN = 1,4,7-trimethyl-1,4,7-triazacyclononane). An assortment of binuclear and mononuclear species has been observed [7,33,34]. One such example focused on the use of these complexes for the oxidative drying of alkyd paints. The binuclear

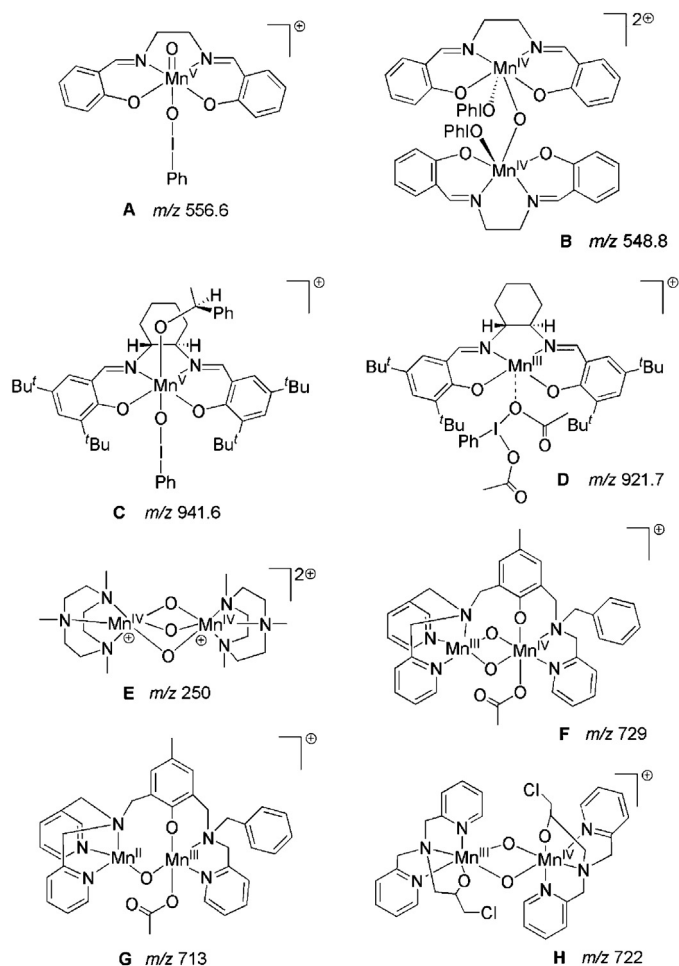
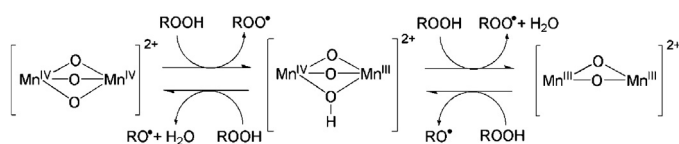


Fig. 1. Manganese-containing species observed by ESI(+)-MS.

complex, $[\text{Mn}_2^{\text{IV}}(\mu\text{-O})_3\text{MeTACN}_2]^{2+}$ (Fig. 1E), was shown to be an effective catalyst; in this case for oxidation of ethyl linoleate (a model complex for alkyd resins) [37]. From a solution of $[\text{Mn}_2^{\text{IV}}(\mu\text{-O})_3\text{MeTACN}_2][\text{PF}_6]_2$ and hydroperoxide, peaks corresponding to the starting material $[\text{Mn}_2^{\text{IV}}(\mu\text{-O})_3\text{MeTACN}_2]^{2+}$ were initially dominant and small peaks corresponding to the mixed valent binuclear system $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}(\mu\text{-O})_3\text{MeTACN}_2]^+$ were present. After 24 h peaks corresponding to the reduced $[\text{Mn}_2^{\text{III}}(\mu\text{-O})_2\text{MeTACN}_2]^{2+}$ dominated the spectrum, consistent with the catalyst acting to decompose hydroperoxides via a reversible equilibrium between $\text{Mn}(\text{IV})_2/\text{Mn}(\text{IV})\text{Mn}(\text{III})/\text{Mn}(\text{III})_2$ (Scheme 1). In alkyd paints this decomposition of hydroperoxides leads to the formation of volatile aldehyde products which aid in the drying of the oil paint.

Isotope labelling experiments are a valuable tool in the mass spectrometrists' mechanistic toolbox for confirming peak assignment and clarifying mechanistic details. For example, the mechanism of peroxide disproportionation by various dimanganese complexes was investigated by Dubois et al. using ESI-MS. Proposed active species of the forms bis(μ -oxo)dimanganese(III/IV)



Scheme 1. Proposed catalytic cycle for the decomposition of hydroperoxide by Mn-MeTACN based on ESI-MS studies.

Modified from reference [37].

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