



Isolation and characterization of a peroxo manganese (III) dioxygen reaction intermediate using cryogenic ion vibrational predissociation spectroscopy

Arron B. Wolk^{a,1}, Christopher M. Leavitt^{a,1}, Joseph A. Fournier^a, Michael Z. Kamrath^{a,2}, Gayan B. Wijeratne^b, Timothy A. Jackson^b, Mark A. Johnson^{a,*}

^a Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, CT 06520, United States

^b Department of Chemistry and Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, KS 66045, United States

ARTICLE INFO

Article history:

Received 31 January 2013

Received in revised form 18 April 2013

Accepted 19 April 2013

Available online 2 May 2013

Keywords:

Peroxo manganese

CIVP

Infrared predissociation

Electrospray ionization

Reaction intermediate

ABSTRACT

We apply cryogenic ion vibrational predissociation (CIVP) spectroscopy to characterize the O₂ attachment motif in a prototypical peroxo manganese (III) reaction intermediate. In this approach, species are extracted from solution using electrospray ionization and cooled in a 30 K ion trap. The infrared spectrum is then obtained by monitoring the photoinduced evaporation of a single, weakly bound N₂ molecule as a function of laser wavelength. Because the resulting CIVP action spectrum is linear in laser fluence, the pattern of well-resolved transitions can be directly compared with harmonic spectra calculated for predicted local minima using density functional theory (DFT). The assignment of the O–O stretching band derived from the activated O₂ ligand is established by following the evolution of the bands with ¹⁸O₂ substitution, and the energy of this transition indicates that O₂ is bound side-on to the Mn center. The successful application of CIVP to this class of compounds opens the way for sensitive spectroscopic characterization of weakly abundant species in complex solution environments.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Structural characterization of metal centers capable of binding and activating O₂ are of interest both to natural and synthetic catalysis [1,2]. For example, Mn-peroxo complexes are likely involved in the mechanisms of Mn catalase and superoxide dismutase reactions, and could even be at play in photosystem II [3–5]. Although considerable effort has been directed toward synthesis and characterization of Mn-peroxo complexes, their structural properties have proven difficult to obtain with traditional methods of analysis (e.g., X-ray, EPR, UV–vis, etc.). For example, while EPR and electronic absorption spectroscopies are routinely used to deduce the overall spin and the electronic state of Mn^{III}–O₂ complexes, these methods yield only indirect information about their geometries [6–15]. When the peroxo species are sufficiently stable to be crystallized, the most detailed structural information comes from X-ray structures, where O₂ has been shown to bind directly to the metal center in a side-on fashion with O–O bond lengths ranging from 1.40 to 1.43 Å [7–9]. Relatively stable peroxo compounds can also be characterized using infrared and Raman spectroscopies [16], where the

O₂²⁻-derived transitions can be identified even in rather congested spectra through ¹⁸O₂ substitution [7,8,12,15]. The ¹⁶O₂ stretch has been observed in five Mn^{III}-peroxo complexes [7,8,12,15,17] with crystallographic data available for four of the five [6–8,15]. The frequency of the O₂ stretches and corresponding O–O bond lengths (when available) are collected in Table 1. The structures of all these compounds are given in Fig. S1. Although resonance Raman has proven to be especially valuable for many organometallic systems, and can be used to isolate minor species in complex mixtures [18,19], it has not been effective for the Mn^{III}–O₂ intermediates due to photo-bleaching upon sample irradiation [9,10].

Because only a few compounds have been explored with traditional analytical methods, the manner in which the ligands affect the O₂ binding motif is poorly understood [20], underscoring the need to develop a new way to rapidly survey more reactive species present as minor components in synthetic mixtures. Such a capability would, for example, dramatically expand our ability to correlate ligand structure with O₂ binding character by allowing rapid access to spectra without labor intensive isolation and work up. Here we address this challenge by exploiting the fact that many of the Mn-peroxo species reported in the literature have been observed as primary ions in mass spectrometric (MS) characterization of synthetic products [9,10,12,14,15,21]. Although MS alone cannot provide detailed structural information, ion structures can be obtained through theoretical analysis of the sharp vibrational spectra available when MS is coupled with spectroscopic probes such as cryogenic ion vibrational predissociation (CIVP) spectroscopy

* Corresponding author. Tel.: +1 203 436 4930; fax: +1 203 432 6144.

E-mail address: mark.johnson@yale.edu (M.A. Johnson).

¹ These authors contributed equally to this work.

² Laboratoire de Chimie Physique Moléculaire, École Polytechnique Fédérale de Lausanne, Lausanne 1015, Switzerland.

Table 1
Measured $\nu_{\text{O-O}}$ frequencies (cm^{-1}) in this work and other “side-on” Mn-peroxo species compared to the analogous O—O bond lengths (\AA) obtained via X-ray crystallography.

| Species | Phase | $\nu_{\text{O-O}}$ frequency (cm^{-1}) | O—O (\AA) |
|---|--------------|---|----------------------|
| $\text{Mn}^{\text{III}}(\text{TPP})\text{O}_2$ [17] | Ar matrix | 983 | 1.421(5) |
| $[\text{Mn}^{\text{III}}(\text{tmc})\text{O}_2]^+$ (this work) | Gas | 970 ± 6 | 1.403(4) [9] |
| $\text{Tp}^{\text{IPr}_2}\text{Mn}^{\text{III}}(\eta^2-\text{O}_2)(\text{im}^{\text{Me}}\text{H})$ [8] | Solid (KBr) | 896 | 1.42(1) |
| $\text{Mn}^{\text{III}}(\text{O}_2)(3,5\text{-iPr}_2\text{pzH})(\text{HB}(3,5\text{-iPr}_2\text{pz})_3)$ [7] | Solid (KBr) | 892 | 1.428(7) |
| $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{QuinoEn}))(\text{OOtBu})](\text{BPh}_4)^+$ [15] | Solid (NaCl) | 888 | 1.457(7) |
| $[\text{Mn}^{\text{III}}(\text{O}_2)\text{H}_2\text{bupa}]^-$ [12] | Solution | 885 | N/A |

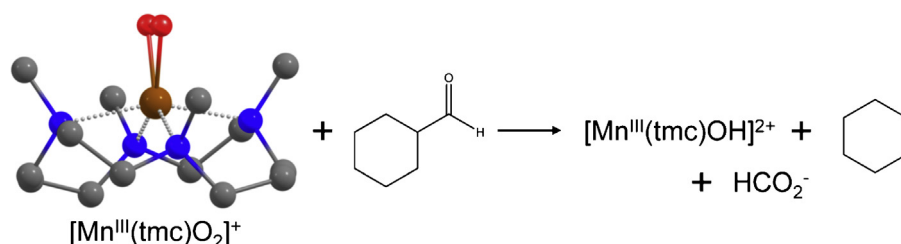
^a This Mn(III)-alkylperoxide complex was determined to be 5 coordinate through X-ray crystallography with a nearly end-on alkylperoxy ligand.

[22–29]. This approach is relatively new and has only been applied to an iridium-based organometallic oxidation catalyst [30] and several activated vanadium-based oxidation catalysts studied in the Asmis group [31,32].

Here we demonstrate the efficacy of the CIVP method for analyzing dioxygen compounds by identifying the O—O stretching fundamental in the $[\text{Mn}(\text{tmc})\text{O}_2]^+$ ($\text{tmc} = 1,4,8,11\text{-tetramethyl-1,4,8,11-tetraazacyclotetradecane}$) complex shown in Scheme 1, which has been shown to be a reactive intermediate in the deformylation reactions of aldehydes [9]. This species was first reported by Nam and coworkers, and was chosen for this demonstration because it is relatively stable at room temperature ($t_{1/2} = 5$ h) and the structure of the ion is known in the CF_3SO_3^- salt by X-ray crystallography [9]. The cation features a side-on peroxo binding motif (Fig. 1a) with an O—O bond length of 1.403(4) \AA . The vibrational frequency was not identified using traditional condensed phase methods, however, and we therefore engaged this collaborative work between Kansas and Yale to obtain the vibrational spectra as a test for the utility of CIVP in this class of systems. The sharp bands recovered for this system using CIVP encode the nature of the O_2 binding motif with great sensitivity, thus offering a new way to characterize activated intermediates in homogeneous catalysis. Having demonstrated the applicability of the method, we discuss extensions of the cryogenic ion chemistry approach that promise a systematic way to form labile intermediates after extraction from solution by gas-phase cluster-mediated condensation [26,33].

2. Experimental methods

CIVP spectroscopy is an action method that yields vibrational spectra analogous to those commonly obtained with FT-IR instruments, but does so on ions extracted from the same ion sources widely used for high resolution mass spectrometry. That is, vibrational spectra can be obtained with comparable sensitivity as MS analysis [9–11,14,15]. In fact, the infrared spectra are often much simpler than those obtained with FT-IR because CIVP necessarily interrogates ions that are held at low temperature (typically 10–30 K) and that are isolated from perturbations due to solvent or counter ions. The overall scheme involves extraction of the ions from a millimolar solution into the gas-phase with an electrospray ionization (ESI) interface, guiding them through differential pumping stages with RF-ion guides into a 90° DC turning quadrupole, and injecting them into a 30 K cryogenic ion trap. Once in the trap, ions are cooled and tagged with N_2 molecules. This is accomplished by pulsing (1–5 ms) a buffer gas mixture into the trap consisting of approximately 10% N_2 in a balance of He. Typical mass spectra of ions extracted from the trap 50 ms after the gas pulse and separated by time-of-flight (TOF) are presented in Fig. 2a and b for the $^{16}\text{O}_2$ and $^{18}\text{O}_2$ isotopologues of $[\text{Mn}^{\text{III}}(\text{tmc})\text{O}_2]^+$, respectively [30]. Though higher volume percentages of N_2 gave larger abundances of the N_2 adduct ions, it greatly decreased signal stability due to condensation of the buffer gas onto the ion trap.



Scheme 1. Aldehyde deformylation catalyzed by $[\text{Mn}^{\text{III}}(\text{tmc})\text{O}_2]^+$. The crystal structure at left indicates the “side on” binding motif of the activated peroxo species.

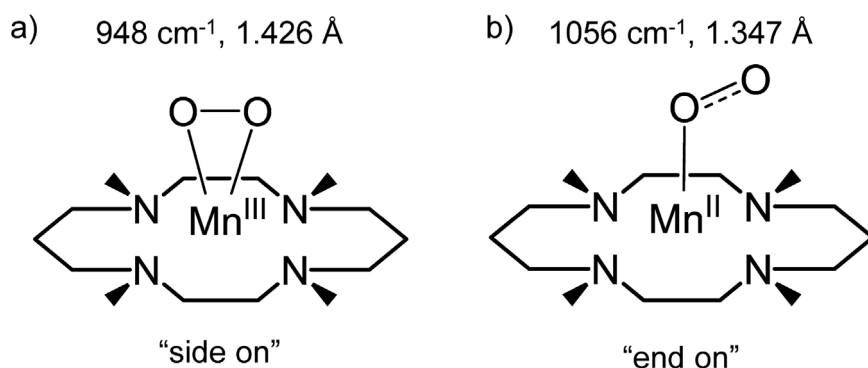


Fig. 1. Schematic structures of the locally stable side-on “peroxo” and end-on “superoxo” O_2 binding motifs in the $[\text{Mn}(\text{tmc})\text{O}_2]^+$ complex. The calculated O—O stretch vibrational quantum and bond length (using BP86/TZVP method/basis set) are indicated below the corresponding structure.

Download English Version:

<https://daneshyari.com/en/article/7605288>

Download Persian Version:

<https://daneshyari.com/article/7605288>

[Daneshyari.com](https://daneshyari.com)