

Oxygen Isotope Effects upon Reversible O₂-Binding Reactions: Characterizing Mononuclear Superoxide and Peroxide Structures

Michael P. Lanci and Justine P. Roth*

Department of Chemistry, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218

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The characterization of intermediates in oxidation reactions of transition metals is a common goal in biological and inorganic chemistry¹ needed to guide the development of new industrial catalysts that can use O₂ as a sacrificial oxidant. Such advances require improved capabilities for identifying metal–O₂ adducts as well as the mechanisms by which these species are formed. In this paper, we examine oxygen equilibrium isotope effects (¹⁸O EIEs) on reversible reactions that give rise to peroxide (O₂²⁻) and superoxide (O₂¹⁻) compounds. The EIEs reported here provide benchmarks for interpreting intermediates during transition-metal-mediated O₂ activation in a variety of natural and synthetic systems.^{2–4}

Classic compounds with defined structures (Chart 1)⁵ were chosen to examine how ¹⁸O EIEs reflect the reduction of O₂ as well as the mode by which it coordinates to a metal center. The observation of O–O stretching frequencies, $\nu(\text{O}–\text{O}) = 800–930 \text{ cm}^{-1}$ for side-on peroxide compounds and $1050–1200 \text{ cm}^{-1}$ for end-on superoxide compounds, has typically served this purpose, although intermediate structures, such as those assigned to side-on superoxide species, have challenged this simple means of classification.⁶ In principle, ¹⁸O EIEs complement existing spectroscopic techniques by reporting on changes in O–O bonding together with the formation of new metal–O bonds.

In this work, ¹⁸O EIEs were determined from the oxygen isotope composition of metal–O₂ adducts that had been pre-equilibrated with natural abundance O₂ from air. A detailed description of the high vacuum apparatus and methodology used for preparing samples has been published.^{2,3b,7} Samples were analyzed by isotope ratio mass spectrometry (IRMS) which gives ¹⁸O:¹⁶O to precisions of ± 0.0002 . The ¹⁸O EIEs were calculated according to eq 1 where R_t is the ¹⁸O:¹⁶O in the “total” O₂ isolated from air-saturated solutions containing the metal–O₂ adduct; R_u is the ¹⁸O:¹⁶O in the “unbound” O₂ from solutions containing only air and $1 - f$ is the fraction of metal-bound O₂ in the air-saturated solutions.

$$^{18}\text{O EIE} = \frac{K(^{16}\text{O}^{16}\text{O})}{K(^{18}\text{O}^{16}\text{O})} = \frac{1 - f}{R_t/R_u - f} \quad (1)$$

Reversibility of O₂ binding is a key requirement for accurate and reproducible determinations of ¹⁸O EIEs. Spurious results occur when metal–O₂ adduct decomposition leads to irreversible consumption of O₂ on the time scale of sample collection. In most experiments, the recovery of O₂ was nearly quantitative at $\geq 22 \text{ }^\circ\text{C}$; yields were determined by manometry and based on concentrations of the metal–O₂ adducts detected by multinuclear NMR and UV–vis spectroscopy.⁷ Using the same methods, equilibrium constants for O₂ binding (K_{O_2}) under 1 atm of dry air were evaluated as a function of temperature in chlorobenzene (CIBz) or dimethylformamide (DMF) (Table 1).⁷

The metal–O₂ adducts in this study are derived from group IX transition metals. Binding of O₂ to square planar Rh^I or Ir^I precursors gives products with side-on peroxide ligands.⁸ These structures are characterized by ¹⁸O EIEs of 2–3% in DMF at 22 °C: 1.0199 \pm 0.0017 (Rh), 1.0226 \pm 0.0013 (Ir_{NCO}), and 1.0305 \pm 0.0023 (Ir_{Cl}).

Chart 1. Structures and Abbreviations of the Compounds Examined

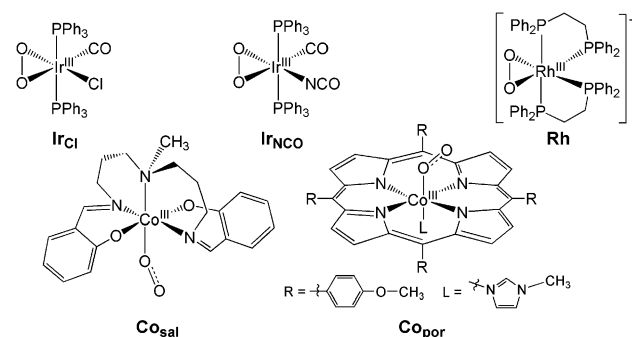


Table 1. Parameters Describing the Reversibility of O₂ Binding

		% yield O ₂ ^a	$K_{\text{O}_2} \times 10^{-3}$ (M ⁻¹) ^a	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (e.u.)
Ir _{Cl}	DMF	82(13)	16(1.9) ^b	-8.4(0.5)	-9.3(3.3)
Ir _{NCO}	DMF	93(10)	1.3(0.30)	-7.3(0.5)	-10(2)
Rh	DMF	90(6)	0.47(0.11)	-15.1(0.8)	-37(3)
Co _{sal}	DMF	97(5) ^c	0.32(0.02) ^c	-13.1(1.0)	-39(7)
Co _{sal}	CIBz	110(19) ^d	0.26(0.05) ^d	-12.4(1.9)	-40(7)
Co _{por}	CIBz	94(14) ^d	0.63(0.21) ^d	-8.9(1.0) ^f	-26(4) ^f

^a Measured at $22 \pm 2 \text{ }^\circ\text{C}$ under 1 atm of dry air unless noted; $\pm 1\sigma$ errors are in parentheses. ^b Estimated from ΔH and ΔS at 22 °C. ^c At -14 °C. ^d At -28 °C. ^e Determined over the following ranges: 40 to 70 °C (Ir_{Cl}), 30 to 60 °C (Ir_{NCO}), 15 to 40 °C (Rh), 0 to -28 °C (Co_{sal}). ^f From ref 5d with errors $\pm 2\sigma$; determined in toluene from -35 to -80 °C.

Binding of O₂ to five-coordinate Co^{II} precursors gives products with end-on superoxide ligands.⁹ Here, lower temperatures were necessary to determine the ¹⁸O EIEs, which are considerably smaller than those quoted above: 1.0041 \pm 0.0011 (Co_{sal}) in DMF at -14 °C, 1.0053 \pm 0.0017 (Co_{sal}) in CIBz at -28 °C, and 1.0066 \pm 0.0013 (Co_{por}) in CIBz at -28 °C. Change in the ¹⁸O EIE for Co_{sal} was undetectable from -28 to 0 °C.⁷

The results for the diverse compounds in solvents of widely varying polarity¹⁰ provide strong evidence that ¹⁸O EIEs are characteristic of the level of O₂ reduction together with the mode by which O₂ binds to the metal (Figure 1). The variation in the observed ¹⁸O EIEs is large considering that the range of calculated ¹⁸O EIEs is 1.00–1.05 for reactions (where O₂ is reduced to HO₂, H₂O₂, H₂O, O₂¹⁻, and O₂²⁻).¹¹ Further, the distinctive ¹⁸O EIEs for side-on peroxide and end-on superoxide structures are in contrast to the expectation of similar ¹⁸O EIEs (~ 1.01) based on an earlier model.¹¹ This model assumed analogous bonding within a metal superoxide species and HO₂ as well as within a metal peroxide species and H₂O₂.

The formalism of Bigeleisen and Goeppert-Mayer¹² is generally used to calculate heavy atom isotope effects in terms of the change in force constants in proceeding from a reactant to a product state. Using this approach, ¹⁸O EIEs of 1.049 (O₂ \rightarrow O₂²⁻) and 1.033 (O₂ \rightarrow O₂¹⁻) are predicted for the reduction of O₂ in the absence of concomitant bond formation (Figure 2). Here the size of the ¹⁸O

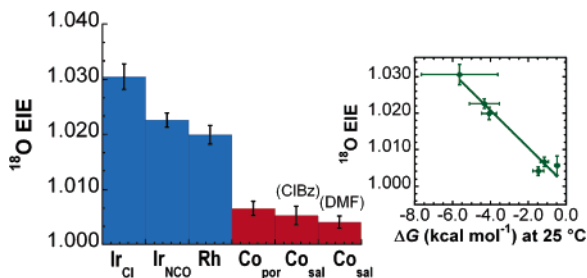


Figure 1. Left: ^{18}O equilibrium isotope effects upon forming the compounds in Chart 1. Right: ^{18}O EIE versus ΔG calculated at 25 °C.

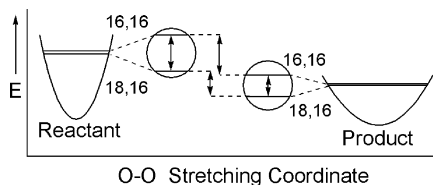


Figure 2. Oxygen isotope effect due to a change in O–O force constant; 16,16 and 18,16 designate zero-point energies of the oxygen isotopologues.

EIE is largely determined by the O–O force constant of the product relative to that of O_2 .²

The ^{18}O EIEs measured for side-on peroxide compounds roughly agree with those calculated using stretching frequencies for the O–O and metal–O normal modes in the above-mentioned approach.³ We have encountered more difficulty matching the experimental results for Co_{sal} and Co_{por} , where calculated ^{18}O EIEs are 1.006–1.017. The variations appear to reflect uncertainties in the low-frequency modes.⁷ The observed ^{18}O EIEs are, however, close to values reported for end-on Fe^{III} superoxide species in heme proteins (1.0039–1.0056). In this original work, the small size of the ^{18}O EIEs was attributed to hydrogen bonding of the terminal oxygen to a nearby amino acid.¹¹ Such effects are unlikely in the present study since the ^{18}O EIEs for Co_{sal} and Co_{por} are indistinguishable in DMF and ClBz, yet only DMF has the ability to form hydrogen bonds.

^{18}O EIEs which characterize the metal– O_2 adducts are likely the result of competing enthalpic and entropic isotope effects,¹³ making Figure 2 an oversimplified view. Weakening of the O–O bond contributes to a normal (>1) isotope effect upon ΔH . Loss of mass-dependent translational and rotational modes when O_2 coordinates to a metal contributes to a normal isotope effect upon ΔS . Offsetting these effects is the formation of new, low-frequency vibrational and rotational modes in the product. The large differences seen for side-on peroxide and end-on superoxide structures suggest that these new modes reduce the ^{18}O EIEs from the values estimated for O_2^{2-} and O_2^{1-} yet do not affect the difference due to the change in O–O force constant. This result would seem counterintuitive because the metal–O modes are also expected to influence the ^{18}O EIE.

The physical origin of ^{18}O EIEs as well as how they relate to ^{18}O kinetic isotope effects (KIEs) will be the subject of future investigations. At this stage, some insight may be gleaned from a comparison of the reactions examined here. If it is assumed that the ^{18}O EIEs for each of the cobalt compounds is the same at 25 °C and the lower experimental temperatures, a trend is observed where the ^{18}O EIE increases as ΔG for O_2 binding becomes more favorable (Figure 1). The result is in contrast to expectations based upon net bonding changes; the formation of two metal–O bonds stabilizes peroxide compounds relative to superoxide compounds. Instead, the trend seems to indicate that the magnitudes of the ^{18}O EIEs are largely determined by changes in the O–O force constant, that is, decreases in $\nu(\text{O}–\text{O})$. Studies of O_2 adducts derived from different

metals and having different bonding geometries are currently in progress to further address this interesting observation.

Insofar as ^{18}O EIEs can be taken as upper limits to ^{18}O KIEs upon unidirectional O_2 binding, the present results support previous studies of O_2 activation by group IX and X metal compounds.^{3a} In this work, we reported ^{18}O KIEs of 1.0069–1.0268 on reactions leading to metal peroxide products. On the grounds that (i) KIEs decreased in proportion to the barriers to O_2 binding and (ii) no intermediate was detectable in any of the reactions, we proposed a single-step mechanism involving a transition state with peroxide rather than superoxide character. Assuming the above ^{18}O EIEs as boundary conditions, a KIE < 1.007 would be expected for a transition state leading to a superoxide intermediate and a KIE < 1.03 would be expected for a transition state leading to a peroxide product. Thus, the observed KIEs appear more consistent with a concerted $2e^-$ mechanism. Of course, a sequential mechanism involving the reorganization of a high-energy superoxide intermediate to a peroxide product in the rate-limiting step cannot be excluded.

In summary, oxygen isotope effects upon reversible O_2 binding to synthetic transition-metal compounds have been determined for the first time. Using defined systems, we have found that the isotope effect is distinctly different when O_2 is bound as a side-on peroxide ligand versus an end-on superoxide ligand to a group IX metal. We suggest the ranges of isotope effects for these compounds can serve as benchmarks for identifying transient metal– O_2 adducts. For example, in cases where outer-sphere electron transfer to O_2 can be ruled out, ^{18}O KIEs of $\sim 1\%$ may signal the intermediacy of end-on superoxide species,^{2,4} whereas values of 2–3% are consistent with peroxide intermediates. This type of analysis provides a new approach to characterizing intermediates in catalytic oxidation reactions.

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Supporting Information Available: A description of the experiments and calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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