

Application of global analysis to linseed oil autoxidation

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Abstract

While the autoxidation of linseed oil has been extensively studied, the role of metal driers in catalyzing this process remains poorly understood. Previous studies have demonstrated that Fourier Transform Infrared spectroscopy (FT-IR) can be used to monitor the progress of autoxidation during linseed oil drying. Typically, studies have focused on a single absorption at 3010 cm⁻¹ to determine the rate of autoxidation. In this study, FT-IR spectra of linseed oil during autoxidation were measured between 3800 and 700 cm⁻¹ and fit to kinetic models using global analysis, which provides more robust fitting than prior methods. This study revealed that the drier catalyzed autoxidation process can be best modeled as an A - B - C type reaction, with B corresponding to a cis-trans conjugated intermediate previously identified in model complex studies. These kinetic models further revealed that for three Co driers the rate constants for the A - B and B - C reactions are identical within experimental error, suggesting both reactions share a rate limiting step.

Introduction

Air-drying coatings consist of at least three main components, a binder which forms the final coating, a solvent that aids in application and uniformity coating, and a drier which catalyzes the conversion of the binder into the coating (Webster 2020). Ongoing interest in sustainable and non-toxic coatings has led to an increasing use of seed oils as binders (Hofland 2012). Seed oils contain unsaturated fatty acids (Fig. 1) which polymerize in the presence of oxygen gas to form solid films. This process, known as autoxidation, is initiated by H-atom abstraction from sites adjacent to olefins generating C-centered radicals (Hubert et al. 1997). While seed oil autoxidation does occur in the presence of oxygen, it typically takes months for binders of this type to fully dry in the absence of a drier. Driers, typically oil-soluble transition metal compounds, catalyze H-atom abstraction allowing solid films to form within hours of application (Bieleman 2002).

Currently, most driers used commercially are based on cobalt. These cobalt-based driers are inexpensive and active at dosages as low as 0.01 wt. % (Charamzová et al. 2018). Recent concerns about potential toxicological and environmental effects of cobalt in driers (Leyssens et al. 2017) have led to efforts to transition from cobalt-based driers to less toxic substitutes, including driers based on manganese (Bouwman and van Gorkum 2007), iron (Křížan et al. 2017), and vanadium (Preininger et al. 2015). To accomplish this transition, a detailed understanding of the drying process is highly valuable.

Many mechanisms have been proposed for the role of the drier in autoxidation (van Gorkum and Bouwman 2005; Soucek et al. 2012; Honzík 2019). One widely invoked hypothesis involves the formation and decomposition of organic peroxides through a Haber-Weiss-type mechanism (Haber and Weiss 1932). In this mechanism low-valent driers reduce organic peroxides by one electron, forming alkoxy radicals (RO^{*}) and hydroxide ions (OH⁻). Subsequently, oxidized driers interact with a second organic peroxide, reducing the metal to its original state and forming peroxy radicals (ROO^{*}) and protons (H⁺) (Fig. 2a). A second mechanism which has been proposed to contribute to radical initiation is peroxide homolysis catalyzed by Co(III) serving as a Lewis acid (Fig. 2b) (Spier et al. 2013). In addition to this mechanism, it has also been proposed that low-valent driers can interact directly with molecular oxygen to generate superoxide (O₂^{*-})

and high valent metal-oxo species (Fig. 2c) (Kumarathasan et al. 1992). Oxidized driers are then reduced to their original oxidation state by reacting with the binder.

Radical species formed through either mechanism, as well as high valent metal species that may be formed, then proceed to abstract H-atoms from bis-allylic methylene sites (Fig. 3, **A**) in the binder. After H-atom abstraction, the olefins rearrange to a conjugated *cis-trans* arrangement (Fig. 3, **B**) and the C-centered radicals react with dissolved oxygen gas or other unsaturated sites in the binder, propagating the radical chain. Further interaction between these newly formed *cis-trans* conjugated species and propagating radicals leads to the formation of isolated *trans*-alkene groups in the binder (Fig. 3, **C**) (Hubert et al. 1997). Details of these mechanisms, including the relative contribution of each of the possible initiation reactions, the importance of dissolved oxygen during propagation, and the role or roles of the drier in propagation and termination have been the subject of extensive computational modeling (Oakley et al. 2018). In order to test the veracity of these proposed mechanisms, more experimental data on the rates of autoxidation using different drier and oil combinations is needed (Orlova et al. 2021).

Drying oil autoxidation is typically studied with Fourier transform infrared spectroscopy (FT-IR) using the method developed by van de Voort (van de Voort et al. 1994). In a typical experiment, the area of the peak centered at 3010 cm^{-1} is measured as a function of time during the autoxidation process. This peak corresponds to an isolated *cis*-alkene stretching mode of the non-conjugated olefins initially present in the drying oil (Fig. 3, **A**). During autoxidation *cis*-olefins isomerize, and the area of the peak at 3010 cm^{-1} decreases in intensity (de Boer et al. 2013). The rate of autoxidation is then determined by performing a linear regression on the peak area as a function of time (Pirš et al. 2014). While this method is generally reliable for determining the rate at which *cis*-alkene groups are consumed, it does not provide information on the other reactions taking place during autoxidation. In particular, this method does not provide information on the formation of *trans*-alkene species (Fig. 3, **C**) related to propagation and termination reactions.

As an alternative to monitoring a single peak in the IR region, we propose the use of global analysis to study drying oil autoxidation rates. Global analysis is a family of mathematical techniques used to find optimal fitting parameters between a model containing multiple unknown variables and the entirety of known experimental data. Global analysis typically begins by applying factor analysis to determine the number of variables contributing to the experimental data (Malinowski 2002). The results of this factor analysis are then combined with knowledge of the system to propose a model, and an iterative optimization algorithm identifies the model parameters which provide the best agreement between the experimental data and the proposed model. In chemistry and biochemistry, global analysis has been widely applied to spectroscopic data to improve the understanding of reaction kinetics in complex systems (Malinowski 2002; van Stokkum et al. 2004). Global analysis is particularly powerful in cases where: a) the spectrum of one or more components cannot be independently measured due to experimental limitations, b) the measured absorbances of one or more components are small relative to other components due to a low concentration and/or low absorptivities, and c) there is significant spectral overlap between the absorbances of different components in the system. Each of these factors is present in the time-resolved FT-IR spectra of drying oil autoxidation, making this process ripe for study using global analysis. In this manuscript, we report the results of our initial application of global analysis to linseed oil drying by cobalt driers.

Experimental Procedures

Cobalt(II) 2-ethyl hexanoate (65 wt. % in mineral spirits), cobalt(II) hexafluoroacetate hydrate, and acetone were purchased from MilliporeSigma and were not further purified. Cobalt(II) acetylacetonate hydrate was purchased from Strem Chemicals and was not further purified. Linseed oil (Supreme quality) was purchased from Cargill and stored under nitrogen. Global analysis was performed using ReactLab Kinetics version 1.1 by Jplus Consulting (Maeder and King 2017).

Sample preparation

Prior to use cobalt driers were dissolved or diluted with acetone in volumetric flasks to a final concentration of 27.2 mM. Linseed oil (1 mL) was added to a vial and stirred under air for 15 minutes. An aliquot of

catalyst solution (0.050, 0.075, or 0.100 mL; 1.36, 2.04 or 2.72 μmol) was added to the aerated oil for a final catalyst concentration of 1.36 mM, 2.04 mM, or 2.72 mM. The oil and drier mixture was stirred for a further 30 seconds before being applied to the IR window via pipette. A uniform film thickness was obtained by running a razorblade over the IR window depression.

FT-IR spectroscopy

All experiments were performed using a Nicolet iS10 FT-IR spectrometer (ThermoFisher Scientific) using the Smart iTX ATR attachment with the following settings: 64 scans, resolution 8, data spacing 0.964 cm^{-1} , range $4000\text{--}600\text{ cm}^{-1}$. Spectra were collected every 20 minutes over a 12-hour period. A background spectrum was collected prior to application of the oil/drier mixture.

Data preparation

Prior to modeling the spectral region between $1900\text{--}2400\text{ cm}^{-1}$ was deleted to remove contributions from CO_2 . Timepoints during the induction period were also removed from the data prior to analysis. The exact timepoints removed for this purpose were determined by plotting the absorbance at 970 cm^{-1} as a function of time. A linear fit with slope zero was applied to the initial data before autoxidation, and a second linear fit was applied to the linear region of increasing peak absorbance. The point at which these fits intersect was defined as $t = 0$ in the model. The first datapoint to fall on the linear region was the first timepoint included in the model. A visual demonstration of this procedure is provided in Fig. S1. Inclusion or exclusion of additional timepoints were found to slightly decrease the overall quality of fit found through global analysis but did not have a significant impact on the species associated spectra (SAS) or rate constants (Fig. S2). Except where otherwise indicated, all spectra shown have been generated from data processed using this procedure.

For single wavelength modeling, the decrease in peak area at 3010 cm^{-1} for each set of data was found by determining the peak area at each time point using OMNIC TQ Analyst software. Once each area was found, the values were normalized so that the area at time 0 was equal to 1. The normalized areas were plotted vs. time and the linear portion of the curve, indicating a steady decrease in area, was identified. The slope of this region was found and determined to be the value of k_{3010} for each experiment, corresponding to the decrease in isolated *cis* double bonds.

Results

Three distinct phases during are observed after drier addition to linseed oil: first, an initial induction period lasting one to two hours; second, the autoxidation period during which low molecular weight polymers form over the course of 3 to 14 hours; and third, a ripening period during which the low molecular weight polymers crosslink over the course of several days to months. During the induction period either no change or a steady, wavelength-dependent increase in IR absorption is observed. This induction period has been previously attributed to oxidation of natural antioxidants in the oil (Orlova et al. 2021). For the purposes of this study, only data from the autoxidation period was included in the global analysis.

Selection of the Model for Global Analysis

The first step in analyzing time-dependent spectral data via global analysis is identifying the number of components, or factors, contributing to the data. For drying oils, IR peaks associated with each of the different olefin configurations found during autoxidation (Fig. 3) have been assigned using model compounds (Muizebelt et al. 1994; Hubert et al. 1997). Several of these peaks are visible in the time-dependent FT-IR spectra of linseed oil during autoxidation by 1.36 mM cobalt(II) hexafluoroacetate hydrate ($\text{Co}(\text{hfac})_2$) as shown in Fig. 4. Specifically, the peaks at 3010 and 723 cm^{-1} are assigned to *cis*-alkene groups initially present in the oil (Fig. 3, **A**); the peak at 985 cm^{-1} is assigned to *cis-trans* conjugated alkene groups formed after initial H-atom abstraction (Fig. 3, **B**); and the peak at 970 cm^{-1} is assigned to isolated *trans*-alkene groups formed via chain propagation and termination (Fig. 3, **C**) (Heredia-Guerrero et al. 2014). Model-free singular value decomposition (SVD) and evolving factor analysis (EFA) confirm the presence of two to four distinct factors contributing to the IR spectra (Fig. S3). Thus, it should be possible to include at least

these three components in the kinetic model. However, each of these IR peaks shows some overlap with other functional groups present in the linseed oil, with overlap particularly severe in the 600-1450 cm^{-1} fingerprint region. Depending on the relative concentrations of each of the different alkene group configurations during autoxidation, this overlap may cause difficulty in uniquely distinguishing one or more of the factors in the kinetic model. To identify the kinetic model most appropriate to the FT-IR data, models containing two, three, and four components and a mix of first and second order rate laws were tested on the FT-IR spectra collected during the autoxidation of linseed oil by 1.36, 2.04 and 2.72 mM $\text{Co}(\text{hfac})_2$.

In line with the currently accepted mechanism, all models including second order rate laws provided very poor fitting to the data and were not further examined. Modeling the 1.36 mM $\text{Co}(\text{hfac})_2$ data using two components, i.e. **A B**, provided a reasonable fit, with the standard deviation of the residuals (σ_r) = 1.0×10^{-3} and the sum-of-squares (ssq) = 1.0×10^{-1} . The largest errors in this two-component model appeared in the carbonyl stretching region near 1790 cm^{-1} and in the fingerprint region (Fig. 5a). The three-component, i.e. **A B C**, model provided a significantly improved fit to this data set, with σ_r = 6.0×10^{-4} and ssq = 2.9×10^{-2} , and greatly reduced error in both the carbonyl stretching and fingerprint regions (Fig. 5b). Furthermore, the predicted species associated spectrum (SAS) for species **B** using this model (Fig. 6b) is distinct, does not appear in the two-component model, and has a peak at 985 cm^{-1} corresponding to the *cis-trans* conjugated intermediate proposed in the currently accepted mechanism (Fig. 3). Inclusion of a fourth component in the model, i.e. **A B C D**, did not significantly improve the fit to this data set, with σ_r = 4.0×10^{-4} and ssq = 1.5×10^{-2} , and exhibited comparable errors in the carbonyl stretching and fingerprint regions. More significantly, inclusion of a fourth component led to features with negative absorptivity constants, a strong indicator of overfitting (Fig. 6c). These behaviors were also seen in the 2.04 and 2.72 mM data sets (Fig. S4). Based on this model testing, the three component **A B C** model was determined to be the most appropriate for fitting the FT-IR spectra of linseed oil during autoxidation.

For each data set, the values of k_1 and k_2 in the **A B C** would begin to converge on the same value, i.e. k_1 [?] k_2 . In order to determine whether k_1 was, in reality, equal to k_2 within experimental error, we further tested a three-component model with the constraint $k_1 = k_2$ using the 1.36 mM $\text{Co}(\text{hfac})_2$ data set. In the model where k_1 and k_2 are optimized freely, values of 6.4×10^{-3} and $7.4 \times 10^{-3} \text{min}^{-1}$ are found for k_1 and k_2 , respectively. When the constraint $k_1 = k_2$ was added, a value of $6.9 \times 10^{-3} \text{min}^{-1}$ was found, with no change in the values of σ_r or ssq. This suggests that allowing k_1 and k_2 to vary independently does not improve the quality of the fit. Furthermore, the residual spectra and SAS generated are effectively identical between the two models, with the only difference being almost imperceptible changes in the molar absorptivities predicted for species **B** (Figs. 7c and 7d). Similar results were observed when these models were applied to the 2.04 and 2.72 mM data sets. Based on these observations, the three-component model with the constraint $k_1 = k_2$ was selected to fit the linseed oil autoxidation data presented in this manuscript. SAS and concentration profiles for all samples studied can be found in the supporting information (Figs. S5 – S13).

Rates calculated from global analysis (k_{fit}) were compared with the rate of decrease in peak area at 3010 cm^{-1} (k_{3010}). As shown in Table 1, greater rate constants are observed using global analysis relative to the single-wavelength model. This is caused by the presence of intensity at 3010 cm^{-1} in the SAS of species **B** and **C** due to the broad peak centered at 2917 cm^{-1} , indicating that the intensity observed at 3010 cm^{-1} is not solely attributable to isolated *cis*-olefins, and suggesting the single-wavelength method underestimates the rate of initiation during linseed oil autoxidation.

Another contrast between the rate constants determined by global analysis and those determined using the 3010 cm^{-1} peak area is seen in the drier concentration dependence. The global analysis model indicates that the maximum rate of autoxidation is found at a concentration of 2.04 mM for each of the three Co driers tested, with lower observed rate constants at both higher and lower concentrations. This is consistent with prior observations that the rate of drying oil autoxidation is inhibited at high catalyst concentrations. Meanwhile, the rate constants derived from measuring the peak at 3010 cm^{-1} show an inconsistent dependence on catalyst concentration, with the maximum rate observed at 1.36, 2.04 and 2.72 mM for $\text{Co}(\text{acac})_2$, $\text{Co}(\text{hfac})_2$ and $\text{Co}(\text{oct})_2$, respectively. Taken together, these differences in rate constants suggest that global

analysis provides a more robust method for determining the rate of linseed oil autoxidation.

Baseline Shift

In several datasets, a wavelength-dependent baseline shift can be observed at the start of the reaction (Fig. 8). This wavelength-dependent increase in absorption occurs during the induction period of autoxidation, and is consistent with light scattering, possibly indicating the formation of nanoparticulate structures in the oil. The extent to which this scattering occurred did not obey any discernable pattern with respect to catalyst identity or concentration, suggesting a complex interplay of factors leads to this light scattering. Possible sources include: a) Co nanoparticles formed from the drier; b) reverse micelles formed from polar oxidation products of the natural antioxidants present in the oil; or c) a mixture of both a) and b). It is not possible to distinguish between these possibilities based on IR data alone, and further analysis of these possibilities is currently underway using model systems. Attempts to normalize the baseline using linear baseline corrections or a penalized least squares smoother (Eilers 2003) were made, but did not lead to any improvement in the global analysis. Despite the interference, global analysis fitting generated reasonable SAS and rate constants, demonstrating the advantages of including data from a wider variety of wavelengths.

Discussion

Use of Global Analysis for Studying Drying Oils

Global analysis demonstrates several advantages over single wavelength analysis for studying drying oils. Firstly, as demonstrated by the 2.72 mM Co(hfac)₂ and 2.04 mM Co(oct)₂ data, diffraction and wavelength dependent baseline drift are intrinsically addressed through the fitting procedure, allowing for analysis of data without the need for pre-treatment and simplifying the overall fitting procedure. Secondly, as demonstrated by the quality of fit to the **A B C** model, including the fingerprint region of the IR in the modeling allows for the identification of intermediate species formed during the drying process that may be difficult or impossible to detect in other regions of the IR spectrum. Finally, the use of global analysis provides a visual representation of the quality of the final fit in the form of residuals, which aids in the identification of places where the model can be further improved.

Both **A** and **C** in these models correspond to those previously identified as the starting and ending species in previous IR studies of linseed oil drying. Specifically, **A** corresponds to bis-allylic C-H sites found in linoleic and linolenic fatty acids (Fig. 1) as evidenced by the peaks at 3010 and 723 cm⁻¹, and **C** corresponds to isolated trans-alkenes formed after isomerization as evidenced by the peak at 970 cm⁻¹. The intermediate species **B** has peaks at 1117 and 985 cm⁻¹, neither of which are present in species **A** or **C**. These peaks are consistently present regardless of the catalyst used but have varying estimated molar absorptivities depending on the identity and amount of catalyst used. This results from limitations of global analysis as described above in the section “Selection of the Model for Global Analysis”.

Mechanistic Implications for Linseed Oil Drying

For each of the samples studied, identical values of k_1 and k_2 were found for the **A B C** model. In addition, the quality of fit and residual spectra improved when the values of k_1 and k_2 were fixed to be equal. This strongly suggests that the air drying of linseed oil is better modeled as two sequential reactions with the same rate constant, rather than a single reaction obeying pseudo first-order kinetics as commonly implemented in the literature. (van Gorkum and Bouwman 2005) While only subtle differences are seen in the single wavelength fittings between these two models, the interpretation of the reaction mechanism and rate determining steps involved in linseed oil drying is changed dramatically.

The one-step model has frequently been interpreted as indicating the rate determining step in the drying process is an H-atom abstraction by the drier, with subsequent steps being too rapid to observe experimentally. This mechanism leads to the rate law: $\text{Rate} = k[\text{Co}][\text{A}]$. In contrast, a two-step model with identical rate constants indicates two identical rate determining steps in the mechanism, with the only difference between the rate laws being the presence of $[\text{A}]$ or $[\text{B}]$.

Two hypothetical mechanisms that would lead to this type of rate law present themselves. In the first, H-atom abstraction by the drier is the rate determining step in both the conversion of **A** to **B** and **B** to **C**. This is equivalent to the rate determining step being initiation and leads to the rate laws: $\text{Rate}_1 = k[\text{Co}][\text{A}]$ and $\text{Rate}_2 = k[\text{Co}][\text{B}]$. This would require similar activation energies for H-atom abstraction from both **A** and **B**. The second possibility is that the rate determining step is the reaction of **A** or **B** with a propagating radical. This is equivalent to the rate determining step being propagation and leads to the rate laws: $\text{Rate}_1 = [\text{R}^*][\text{A}]$ and $\text{Rate}_2 = [\text{R}^*][\text{B}]$. This mechanism requires the activation energies for radical attack on olefin groups in both **A** and **B** to be similar.

We currently favor the latter hypothesis as an explanation for the observed kinetic data for three reasons. First, it can explain the induction periods seen in the drying of linseed oil as the time needed not only to consume natural antioxidants (Orlova et al. 2021), but also build up a steady-state concentration of propagating radicals. Secondly, a rate dependence on steady-state radical concentration is consistent with the observed rate dependence on drier concentration. Specifically, in this mechanism the drier affects the drying rate indirectly through the steady-state concentration of propagating radicals by affecting initiation and termination reactions. Previous studies have suggested the driers can catalyze both initiation and termination reactions, consistent with this hypothesis (van Gorkum and Bouwman 2005; Charamzová et al. 2018). Finally, it makes logical sense that a radical attack on an alkene group in either **A** or **B** would have comparable activation energies, and therefore rate constants, while different activation energies would be expected for H-atom abstraction from **A** or **B**.

Conclusions

Global analysis provides a relatively simple and robust alternative to single-wavelength decomposition as method for analyzing the drying progress of air-drying coatings. By applying this technique to data collected on linseed oil using several related driers, we were able to identify and track the formation a cis-trans conjugated intermediate during the drying process, which was previously predicted to form based on studies of model complexes. Our observations of the formation and consumption of this intermediate indicate identical rate constants for these reactions, strongly suggesting the same fundamental reaction for both steps. To the best of our knowledge, no mechanisms incorporating this possibility have been previously proposed in the literature (Orlova et al. 2021). Our hope is that application of global analysis to studies of drying oils, both future and existing, will enable more insights into the mechanism of this critical process.

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Authorship

A.J.K. carried out the research. A.R.P conceived of and designed the study. Both authors contributed to data analysis, and contributed to and approved of the final draft of the manuscript.

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Fig. 1 Lewis structures of fatty acids commonly found in drying oils. Fatty acids may be present as both triglycerides and free acids.

Fig. 2 Proposed mechanisms for radical initiation by transition metal driers.

Fig. 3 Olefin structural motifs formed during drying oil autoxidation: **A** , non-conjugated *cis* -olefins with a methylene spacer; **B** , *cis-trans* conjugated olefins formed upon rearrangement after initial H-atom abstraction; **C** , isolated *trans* -olefins formed from termination reactions.

Fig. 4 FT-IR spectra of linseed oil mixed with 1.36 mM Co(hfac)₂ collected at 1-hour intervals for 12 hours. Initial timepoint corresponds to 2 hours.

Fig. 5 Residual spectra (dark to light with respect to time, initial and final spectra shown in red and purple respectively) for 1.36 mM Co(hfac)₂ sample fit using a) **A B** model, b) **A B C** model, and c) **A B C D** model over 13 hours. For each plot, induction period is 80 minutes and first time point shown is 120 minutes while subsequent time points are 20 minutes apart.

Fig. 6 Species associated spectra (SAS) for species **A–D** (blue, orange, black, and green respectively) from global analysis of 1.36 mM Co(hfac)₂ fit with a) **AB** model, b) **A B C** model, and c) **A B C D** model.

Fig. 7 Residual spectra (dark to light with respect to time, initial and final spectra shown in red and purple respectively), and SAS (blue, orange, and black correspond to species **A** , **B** , and **C**) of global fits for 1.36 mM Co(hfac)₂ in linseed oil, when k_1 and k_2 are unrestricted (a, c) and k_1 is fixed as equal to k_2 (b, d).

Fig. 8 a) Raw spectra and b) predicted SAS (**A** blue, **B** orange, **C** black) for the autoxidation of linseed oil containing 2.04 mM Co(acac)₂ drier.

Table 1. Calculated rate constants and statistical parameters for global fits of linseed oil oxidation with Co(acac)₂, Co(hfac)₂, and Co(oct)₂.

Concentration	$k_{\text{fit}}^{\text{a}}$ (min ⁻¹)	k_{3010}^{b} (min ⁻¹)	σ_{r}	ssq
Co(acac) ₂ 1.36 mM	6.1*10 ⁻³	2.6*10 ⁻³	0.003	0.907
Co(acac) ₂ 2.04 mM	1.1*10 ⁻²	2.2*10 ⁻³	0.004	1.38
Co(acac) ₂ 2.72 mM	2.6*10 ⁻³	2.0*10 ⁻³	0.002	0.207
Co(hfac) ₂ 1.36 mM	6.9*10 ⁻³	3.2*10 ⁻³	0.0006	0.0286
Co(hfac) ₂ 2.04 mM	7.6*10 ⁻³	5.7*10 ⁻³	0.0006	0.0306
Co(hfac) ₂ 2.72 mM	6.7*10 ⁻³	3.6*10 ⁻³	0.0015	0.1440
Co(oct) ₂ 1.36 mM ^c	6.3*10 ⁻³	2.7*10 ⁻³	0.0016	0.2411
Co(oct) ₂ 2.04 mM ^d	9.1*10 ⁻³	1.9*10 ⁻³	0.0026	0.4750
Co(oct) ₂ 2.72 mM	6.8*10 ⁻³	2.8*10 ⁻³	0.0008	0.0542

^a k_{fit} represents the fixed rate constant, where $k_1 = k_2 = k_{\text{fit}}$; found from previous global fits to the same data set.

^b k_{3010} represents the normalized rate of the decrease in peak area for the peak centered at 3010 cm⁻¹.

^c Species **C** fixed as final spectrum from experiment before fitting.

^d Species **A** fixed as initial spectrum, and species **C** fixed as final spectrum from experiment.





