Long Wavelength Photochemistry of Ozone and n-butylferrocene: a Matrix Isolation Study

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Abstract

The photochemical reaction of ozone and n-butylferrocene has been studied using a combination of argon-matrix isolation, infrared spectroscopy, and theoretical calculations. The dark deposition produced a vivid green matrix that, when irradiated with red light, turned a brownish-red color. This green matrix as well as slightly red-shifted O_3 infrared absorptions are indicative of the formation of an initial charge transfer complex between ozone and n-butylferrocene. The spectral results support the photodissociation of the complexed ozone with red light ($\lambda \geq 600$ nm) producing an oxygen atom, $O(^3P)$, and a dioxygen molecule, $O_2(^3\Sigma)$. The $O(^3P)$ then reacts with n-butylferrocene to form products consisting of an iron atom with a coordinated n-butylcyclopentadienyl or cyclopentadienyl ring and either: (1) a pyran, (2) an aldehyde, or (3) a bidentate cyclic aldehyde with a seven-membered ring including the iron atom. The photochemical products were characterized with FT-IR spectroscopy, ^{18}O -labeled O_3 experiments, and DFT calculations using the B3LYP functional with the 6-311++G(d,2p) basis set. A possible mechanism for the photochemical reaction is discussed.

Keywords: matrix isolation, infrared spectra, theoretical calculations, photodissociation, oxidation, mechanism

Introduction

The use of organometallic compounds such as ferrocene as precursors for the formation of metal oxide thin films has become an area of intense study over the last decade.¹⁻⁵ In general, metal oxide thin films play an important part in our lives; they are used in flat panel displays, energy saving window coatings, solar cells, and a variety of other devices.⁶⁻⁸ Thin films are primarily generated by techniques such as atomic layer deposition (ALD), chemical vapor deposition (CVD) or physical vapor deposition (PVD).⁹⁻¹¹ PVD techniques, such as evaporation or sputtering, involve the adsorption of the vaporized material onto the substrate to form the thin film.⁹ CVD is a process that involves the formation of a thin film of solid reaction product on a substrate by the reaction of gas phase precursors.^{10,11} In CVD, metal oxide thin films are often prepared by reacting a volatile organometallic compound with an oxygen source.¹¹ Increasingly, ozone is being used as the oxygen source because it has a high oxidation potential, it contains only oxygen and it is volatile, leading to rapid and effective metal oxide thin film formation.¹²⁻¹⁵

Thin films containing iron oxide have been of particular interest and the subject of numerous research papers. They have been used in photochemical cells, batteries, and gas sensors.¹⁶⁻²¹ Metallocenes are one class of iron precursors used in the CVD of iron-oxide-containing thin films.² This class includes ferrocene (Cp_2Fe) and n-butylferrocene (n-butyl Cp_2Fe), which have been investigated for use as an iron precursor in CVD.^{1,2,22} n-Butylferrocene, like ferrocene, has several advantages over other iron precursors since it is relatively inexpensive, thermally stable, neither air nor moisture sensitive, and vaporizes cleanly. n-Butylferrocene has also been used in CVD as a co-precursor with nickelocene and oxygen to

form a thin film of nickel ferrite (NiFe_2O_4). The nickel ferrite thin film is of particular interest due to its potential for application in microelectronic devices.²²

Recently a matrix isolation study of the reaction of ferrocene (cp_2Fe) and ozone (O_3) was conducted by Kugel et al.²³ This study used matrix-isolation combined with IR spectroscopy and theoretical calculations to show that a photochemical reaction of O_3 with cp_2Fe occurs upon irradiation with red light ($\lambda \geq 600 \text{ nm}$). This low-energy photochemical reaction leads to the production of atomic oxygen $\text{O}(^3\text{P})$ which subsequently reacts with cp_2Fe resulting in the formation of an iron cyclopentadienyl ring moiety and ether: (1) a pyran, (2) an aldehyde, or (3) a bidentate cyclic aldehyde with a seven-membered ring including the iron atom. It should be noted that a dark green matrix was observed prior to irradiation and this color was attributed to a charge transfer complex between O_3 and cp_2Fe ($\text{cp}_2\text{Fe}-\text{O}_3$). The present work investigates the photochemical reaction of O_3 with n-butylferrocene (n-butyl cp_2Fe), and it explores the effect of the n-butyl substituent on the reaction and the observed products. The study was done using the low-temperature technique of matrix-isolation combined with FT-IR spectroscopy and theoretical calculations. Matrix-isolation has the potential to trap and stabilize reactive species, such as early intermediates, and allows for their characterization by spectroscopy.

Experimental Section

Ozone (O_3) was produced by the Tesla coil discharge of molecular oxygen (O_2) (Wright Brothers) while being condensed with liquid nitrogen. Excess O_2 was pumped off prior to the ozone being warmed to room temperature. The O_3 was then transferred to a mixing can where it was diluted with argon (Ar) (Wright Brothers, 99.998%) in an Ar/ O_3 ratio of ≈ 250 . Stock n-butylferrocene (n-butyl cp_2Fe) (Strem Chemicals, 99%) was purified by sublimation. The n-butyl cp_2Fe was placed in a sample holder that was heated with a sand bath at a temperature of

~45°C causing vaporization. The sample holder was attached by an Ultra-Torr® tee to the deposition line where the vaporized n-butyl cp₂Fe mixed with pure argon. All experiments were conducted using a standard matrix isolation system and the twin jet (TJ) configuration as previously described.²⁴ The matrix was deposited in the dark onto a CsI cold window over 24 hours and deposition was stopped prior to the collection of the first spectrum. Spectra were collected with a Perkin-Elmer Spectrum One infrared spectrometer at 1 cm⁻¹ resolution. In order to minimize the exposure of the matrix to the spectrometer source prior to irradiation, the windows were covered during deposition. The matrix was then irradiated using the output from an incandescent light bulb filtered through a red glass cutoff filter (Corning red glass filter #2418, transmits $\lambda \geq 600$ nm) or an infrared cutoff filter (Schott infrared glass filter RG1000, transmits $\lambda \geq 1000$ nm) for 30 minutes each. Spectra were collected after each irradiation.

Computational Details

The calculations were performed with the Gaussian 09 suite of programs²⁵ using density functional theory (DFT), at the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional and with the 6-311++G(d, 2p) basis set. Complete geometry optimizations, infrared vibrational frequencies, and energies for all species and were obtained at this level of theory, a level that has been shown to be a cost effective way to successfully predict the structures and properties of the species of interest. Transition states and IRC calculations were also done at this level. This method provides calculated infrared vibrational frequencies within $\pm 3\%$ agreement with the experimentally observed bands and ¹⁸O-isotope shifts within ± 2 cm⁻¹ of the experimentally observed shifts. Charge distribution results are from natural bond orbital (NBO) analyses of the optimized species.

Results and Discussion

Blank spectra including deposition, annealing, and irradiation were obtained for both parent compounds in argon prior to conducting codeposition experiments. These blanks showed excellent agreement with both literature and calculated spectra.^{26,27} A list of the calculated infrared vibrational frequencies and intensities for n-butyl cp₂Fe is provided in Table S1a. The calculated ring conformation of n-butyl cp₂Fe is eclipsed (Figure 1a) and a stable staggered conformation could not be located. The calculated eclipsed conformation for n-butyl cp₂Fe is consistent with that of the experimentally determined gas phase structures of methylferrocene and ethynylferrocene.^{28,29}

Figure 1 (a) Gaussian optimized structure of n-butylferrocene. (b) The charge density of and the designations for the n-butyl cp₂Fe ring carbons.

Early results of the Ar/O₃ and Ar/n-butyl cp₂Fe twin jet (TJ) deposition experiments indicated that a photochemical reaction occurs upon exposure to light from the He/Ne calibration laser ($\lambda = 632$ nm) or the IR source. The exposure to light from the IR spectrometer resulted in a change of the color of the matrix at the point where the calibrating laser and IR source passed through. This phenomenon was also observed in the Ar/O₃/cp₂Fe experiments.²³ All further experiments were performed by covering the cell windows during deposition.

Dark Deposition. No product bands were observed in the twin-jet, dark deposited spectrum of Ar/n-butyl cp₂Fe + Ar/O₃, other than slightly red-shifted ozone absorptions (Figure S1). The matrix formed during the dark deposition was also a distinct green color (Figure S2a) whereas the colors of the Ar/O₃ and Ar/n-butyl cp₂Fe matrices formed during the collection of the blanks were clear and pale yellow respectively. Annealing the matrix to 36 K did not lead to the formation of any product peaks nor any change in color of the matrix. A similar green matrix was also previously formed in the dark deposition of Ar/cp₂Fe/O₃, and the green color there was attributed to a cp₂Fe-O₃ charge transfer complex.²³ Evidence for the formation of these charge transfer complexes was based on the green color, suggesting strong red and blue absorptions in the visible spectrum, and slightly red-shifted ozone absorptions that are characteristic of perturbed ozone.³⁰ Recently, a UV-vis study³¹ of the O₃/cp₂Fe and O₃/n-butyl cp₂Fe systems led to the observation of a strong, broad electronic absorption in the 750 – 820 nm region for each system. Based on time-dependent DFT calculations, these bands were assigned to a 1:1 complex of O₃ with cp₂Fe and n-butyl cp₂Fe. Thus, we conclude that the green color of the matrix observed here and the shifted ozone vibrational bands are due to a 1:1 complex of O₃ with n-butyl cp₂Fe.

Photochemical Reaction. When the matrix was irradiated using the output from an

incandescent light bulb filtered through a red glass cutoff filter (transmitting $\lambda \geq 600$ nm) a number of product bands were observed (Figure 2).

Figure 2 Infrared absorption spectra (a) (535-1150 cm^{-1}), (b) (1350-1490 cm^{-1}), and (c) (1570-1700 cm^{-1}) of: Ar/ $^{16}\text{O}_3$ /n-butylferrocene matrix after 1 hour red ($\lambda \geq 600$ nm) irradiation (red trace), dark deposited Ar/ $^{16}\text{O}_3$ / n-butylferrocene (green trace), Ar/ n-butylferrocene (black trace), Ar/ $^{16}\text{O}_3$ (pink trace), and Ar/ $^{18}\text{O}_3$ /n-butylferrocene after 30 min. red ($\lambda \geq 600$ nm) irradiation (blue trace). Peak assignments: P = pyran, A = aldehyde, R = ring-aldehyde, U = unassigned.

Diagnostically significant product peaks were located in the C=O stretching region at 1681 cm^{-1} and in the C–H stretching region at 2712 cm^{-1} . Several product peaks were also observed in the C–O–C stretching region. In addition to the formation of product peaks upon irradiation, a change in the color of the matrix from vivid green to red-orange was observed. Photographs of the green dark-deposited Ar/n-butyl $\text{cp}_2\text{Fe}/\text{O}_3$ matrix prior to irradiation with red light and resulting red-orange matrix post irradiation are provided in the supplementary information (Figure S3). There are many similarities in the product peaks and color changes observed in both the Ar/n-butyl $\text{cp}_2\text{Fe}/\text{O}_3$ and Ar/ $\text{cp}_2\text{Fe}/\text{O}_3$ spectra after the irradiation with red light.²³

It has been documented in the literature that excitation of the Chappuis band ($420 \text{ nm} \leq \lambda \leq 700 \text{ nm}$) leads to the photodissociation of O_3 .^{30,32} Furthermore, Kugel, et al. observed isotope scrambling between $^{18}\text{O}_3$ and $^{16}\text{O}_2$ co-isolated in an Ar matrix after irradiation with red light ($\lambda \geq 600 \text{ nm}$).²³ The irradiation of O_3 with red light ($\lambda \geq 600 \text{ nm}$) produces atomic oxygen, $\text{O}(^3\text{P})$, and molecular oxygen, $\text{O}_2(^3\Sigma)$. The $\text{O}(^3\text{P})$ produced by red photolysis of O_3 has up to +23 kcal/mol of excess thermal energy.³³ Calculations done during the vis/UV study of this system demonstrate a significant enhancement of the intensity of the long-wavelength of absorption of O_3 in the 1:1 complex with n-butyl cp_2Fe , leading to enhanced $\text{O}(^3\text{P})$ formation. The photochemical products observed here are proposed to be the result of a reaction between $\text{O}(^3\text{P})$ and n-butyl cp_2Fe and not those of O_3 and n-butyl cp_2Fe .

Based on the products observed in the literature for reactions of $\text{O}(^3\text{P})$ with alkenes, the

spectral similarities to the previous study of Ar/cp₂Fe/O₃, and the diagnostically significant peaks observed in the spectrum of irradiated Ar/n-butyl cp₂Fe/O₃, several possible products were proposed.^{23,34-38} These proposed products consist of an iron atom with a coordinated n-butylcyclopentadienyl (nBuCp) or cyclopentadienyl (Cp) ring and either: (1) a pyran, (2) an aldehyde, or (3) a bidentate cyclic aldehyde with a seven-membered ring including the iron atom. However, in the case of n-butyl cp₂Fe the butyl group on one of the Cp rings means that there are multiple regioisomers of the pyran (pyran-A–F), aldehyde (ald-A–I), and *ring*-aldehyde (*r*ald-A–E); as well as a ketone (*k*eto) and *ring*-ketone (*r*keto) to consider. In addition, two conformational isomers of the aldehyde were also calculated. The two configurations are designated by the position of the hydrogen on the aldehyde group relative to the hydrogen or n-butyl group on the adjoining carbon atom. The aldehyde with oxygen atom pointing outwards and the hydrogens (or the n-butyl group and hydrogen) opposite of each other is designated the (E)-aldehyde (Figure 3a). The aldehyde with oxygen atom pointing inward and the hydrogens (or the n-butyl group and hydrogen) on the same side is designated the (Z)-aldehyde (Figure 3b). Table S1 (in the supplementary information) gives calculated infrared vibrational frequencies, infrared intensities, and ¹⁸O-isotopic shifts of selected examples of these products.

a) (E)-ald-A

b) (Z)-ald-A

Figure 3 E/Z conformational isomers of aldehyde-A (ald-A). (a) The E conformation of Ald-1 with the hydrogen of the aldehyde group and n-butyl group (or the hydrogen, in the case of the other aldehydes) of the adjoining carbon are on opposite sides. (b) The Z conformation of ald-A with the hydrogen of the aldehyde group and n-butyl group (or the hydrogen, in the case of the other aldehydes) of the adjoining carbon are on same sides.

Products formed from the reaction of $O(^3P)$ with the butyl group were not considered, given the presence of the conjugated cyclopentadienyl ring. The literature suggested that alkyl substituent makes the reaction of atomic O with the unsaturated carbons more favorable.³⁷ The reaction of $O(^3P)$ with alkenes was reported to occur through the addition of the O atom to a carbon of the double bond.^{34,37,38} The mechanism proposed and supported by theoretical

calculations for the reaction of cp_2Fe and $\text{O}(^3\text{P})$ involves the addition of $\text{O}(^3\text{P})$ to one of the ring carbons to form a biradical species where the oxygen atom is bound to one of the carbons in the cyclopentadienyl ring. This species then subsequently reacts to form the photo-products observed in the matrix.²³ The mechanism proposed for the reaction of n-butyl cp_2Fe and $\text{O}(^3\text{P})$, discussed in detail in the following section is consistent with the formation of a biradical species in which the oxygen atom is bound to one of the ring carbons as the precursor for the products observed in the matrix after irradiation. A natural bond orbital (NBO) analysis of n-butyl cp_2Fe shows that the charge density on the ring carbons is not uniform, as shown in Figure 1b. The ring carbon (C1) with the n-butyl substituent has a significantly lower negative-charge density than the other ring carbons. As a result it is unlikely that the electrophilic oxygen atom would bond to the C1 to form a biradical species. Furthermore, in reactions of atomic oxygen with alkenes, the preference for the initial oxygen atom to attack to occur at the least substituted carbon atom has been documented in the literature.³⁸ This makes the formation of the ketone (keto) or *ring*-ketone (*rketo*), resulting from the initial formation of C1 biradical species, unlikely.

The calculated infrared vibrational frequencies and ^{18}O -isotopic shifts for each of the n-butyl cp_2Fe pyran regioisomers show substantial similarities to one another. These similarities are also observed when comparing the calculated results of the n-butyl cp_2Fe aldehyde regioisomers and structural isomers to each other. Given the uncertainty associated with the calculated spectra and ^{18}O -isotopic shifts, the calculated spectra do not allow for the distinction between regioisomers of a given pyran or aldehyde based on spectroscopy. However, some of the *ring*-aldehyde regioisomers' calculated spectra do show some significant differences that can be used to eliminate some from consideration. Both *rald*-A and -D are calculated to have intense peaks with ^{18}O -isotopic shifts which were not observed in the irradiated experimental spectra.

Figure 2 show spectra of the TJ-dark-codeposited matrix of O₃ and n-butyl cp₂Fe in argon after red irradiation and Table 1 lists the product peaks and assignments. It is likely that multiple regioisomers of each species are present in the matrix. Thus, assignments of product peaks are made to a group of regioisomers and not to a specific member of that group. However, for comprehensibility of the table only the calculated vibrational frequencies and ¹⁸O-isotopic shifts of the regioisomer that best matches the assigned peak are given in Table 1.

Table 1 Band Positions and Assignments for the Products from the Twin Jet Deposition of Ozone with n-Butylferrocene upon Irradiation with Light of $\lambda \geq 600$ nm.

exptl bands ^a	calcd bands ^b	¹⁸ O		assignments
		calcd shift ^b	exptl shift	
551 (m)	559	-6	-7	pyran
781 (m)	755	0	-1	<i>ring</i> -aldehyde
846 sh (vw)	841	0	0	aldehyde
889 (m)	894	-4	-6	pyran
927 (s)	956	-7	-8	pyran
945 (vw)	961	-11	-13	pyran
959 (vw)			-4	
1078 (m)	1091	-5	-4	pyran
1135 (vw)			-8	
1140 (m)	1160	-4	-5	pyran
1164 (vw)	1199/1196	-2/0	-1	pyran/aldehyde
1360 (vw)	1330	-1	0	<i>ring</i> -aldehyde
1372 (vw)	1339	-2	-3	<i>ring</i> -aldehyde
1440 (m)	1455/1465	0	0	aldehyde/ <i>ring</i> -aldehyde
1471 (w)	1512/1471, 1474	0	0	pyran/ <i>ring</i> -aldehyde
1583 (m)	1608	-6	-6	<i>ring</i> -aldehyde
1680 (vs)	1747	-35	-27	aldehyde
2712 (m)	2902	0	0	aldehyde

^a Frequencies in cm⁻¹

^b Calculated at the B3LYP/6-311G++(d,2p) level of theory, unscaled.

Reaction Mechanism. The proposed photochemical reaction between n-butyl cp₂Fe and O₃ starts with production of ground state atomic oxygen with up to as much as +23 kcal/mol of excess thermal energy by photolysis at $\lambda \geq 600$ nm, as discussed in the previous section.³³ Based on the products observed in the spectra after irradiation and literature for reactions of O(³P) with alkenes³⁴⁻³⁷ a possible general reaction of O(³P) and n-butyl cp₂Fe is shown in Scheme 1:

Scheme 1. Proposed general scheme for the ($\lambda \geq 600$ nm) photochemical reaction between O(³P) and n-butyl cp₂Fe.

- (2) $\text{O}(^3\text{P}) + \text{n-butyl cp}_2\text{Fe} \rightarrow \text{n-butyl cp}_2\text{Fe-O (biradical)} \rightarrow \text{n-butyl cp}_2\text{FeO (aldehyde)}$
- (3) $\text{n-butyl cp}_2\text{FeO (pyran)} \rightarrow \text{n-butyl cp}_2\text{FeO (aldehyde)}$
- (4) $\text{n-butyl cp}_2\text{FeO (aldehyde)} \rightarrow \text{n-butyl cp}_2\text{FeO (ring-aldehyde)}$

The $\text{O}(^3\text{P})$ can react with n-butyl cp_2Fe to form either a pyran (1) and an aldehyde (2). The aldehyde can then subsequently form the *ring*-aldehyde (4). Reaction (4) is based on the presence of infrared peaks assigned to the *ring*-aldehyde after red photolysis ($\lambda \geq 600 \text{ nm}$) which are not significantly present after infrared photolysis ($\lambda \geq 1000 \text{ nm}$). Reaction (3) is the conversion of the pyran through a ring opening to form the aldehyde. Although the average energy of the aldehyde is 11 kcal/mol higher than the average energy of the pyran, reaction (3) could still be possible given the excess energy available from the initial exothermic formation of the pyran product. Figure 4 gives the reaction potential energy diagram for the formation of pyran-A, reaction (1) and ald-A, reactions (2) and (3).

Figure 4 Calculated potential energy diagram for n-butyl cp₂Fe + O(³P) → pyran-A + ald-A. [n-butyl cp₂Fe + O(³P)] = uncomplexed n-butyl cp₂Fe and O(³P); [1T] = a triplet van der Waals complex between n-butyl cp₂Fe + O(³P); [ts1T] = transition state 1 for the formation of the triplet biradical; [2T] = triplet biradical; [2S] = singlet biradical; [ts2S] = transition states connecting singlet biradical with singlet epoxide. [3S] = singlet epoxide; [ts3S] = transition states connecting singlet epoxide with singlet pyran-A; [4S] = singlet pyran-A; [ts4S] = transition state connecting singlet pyran-A, [4S], with the singlet aldehyde; [5S] = singlet aldehyde; [ts5S] = transition state connecting biradical, [2S], with singlet aldehyde, [5S]. The energies* and structures of the epoxide, [3S], and the transition states, [ts3S] connecting singlet epoxide with singlet pyran-A are derived from the an IRC calculation.

The calculated structures corresponding to potential energy diagrams are given in Figure S3. The calculated structures suggest that the transition states are accessible once O(³P) is formed via irradiation with $\lambda \geq 600$ nm and that the reactions (2) and (3) involve a stable but unobserved biradical [2T→2S] and an epoxide [3S]. The diagram starts with addition of O(³P) to carbon 2 (C2) to form a triplet van der Waals complex (T-vdW-C2), [1T]. The calculations show that these species can react in an essentially barrierless exothermic reaction to form a triplet biradical (T-BR-C2), [2T]. This triplet biradical can undergo an intersystem crossing to form the corresponding singlet biradical (S-BR-C2), [2S]. The S-BR-C2, [2S], can rearrange to yield an epoxide (S-epox-A), [3S]. The epoxide can undergo further rearrangement to form the pyran (pyran-A) from reaction (1). It should be noted that although a stable S-epox-A could not be located, evidence for its transitory presence comes from the IRC calculated for the transition of S-BR-C2 to pyran-A. This is likely due to a low activation energy barrier for the formation of pyran-A. The energies and structures given for [3S] and [ts3S] in Figure 4 are derived from the IRC calculation and the IRC is provided in Figure S4. In addition to forming pyran-A, S-BR-C2, [2S], can also rearrange to yield an aldehyde (S-ald-A), [5S], by reaction (2), and this rearrangement has an activation barrier of 11.3 kcal/mol. Pyran-A can also undergo a ring opening to form ald-A by reaction (3), and that this reaction has an activation energy barrier of 21.0 kcal/mol. The mechanism proposed for reaction of n-butyl cp₂Fe and O(³P) is complicated by the multiple regioisomers of each product. The full reaction mechanism proposed when O(³P) reacts with C2 to form (T-vdW-C2) is given in Figure 5. It proposes that S-BR-C2, [2S], can

also form pyran-B, ald-B, and rald-B. These pathways indicate that reactions (1) – (4) and the regioisomers of products may be connected by an unobserved singlet biradical. *r*ald-A was not listed as a product since it was previously established not to be present in the matrix based on its calculated IR spectrum.

Figure 5 The full reaction scheme proposed when $O(^3P)$ reacts with C2 of n-butylferrocene to form T-vdW-C2.

The formation of the photochemical products' remaining regioisomers are proposed to follow the same reaction mechanism discussed above; which starts with addition of $O(^3P)$ to a carbon in either ring of n-butyl cp_2Fe to form a triplet van der Waals complex (T-vdW). However, the formation of a T-vdW complex involving the C1 carbon is unlikely given that this ring carbon is calculated have a significantly lower charge density than the other ring carbons (Figure 1b). As a consequence the formation of resulting ketone (keto) and *ring*-ketone (*rketo*) would be unlikely. Although the formation of the keto and *rketo* cannot be totally eliminated as they could be formed from pyran-A via reactions (3) and (4) they would likely not be significant products. The mechanism of the reaction resulting in the formation of regioisomers involving

cyclopentadienyl ring carbons (C6-C10) of n-butyl cp₂Fe (pyran-D –F, ald-E –I, and *rald*-E) are proposed to follow the same mechanism as that given for cp₂Fe and O(³P).²³

Conclusions

There is strong evidence that upon irradiation with $\lambda \geq 600$ nm the initial step in the photochemical reaction of n-butyl cp₂Fe and O₃ is photodissociation of O₃. This yields a highly reactive atomic oxygen, O(³P), and molecular oxygen, O₂(³Σ). O(³P) reacts with n-butyl cp₂Fe to produce the observed photochemical products. These products contain an iron atom with a coordinated n-butylcyclopentadienyl or cyclopentadienyl ring and either: (1) a pyran, (2) an aldehyde, or (3) a bidentate cyclic aldehyde with a seven-membered ring including the iron atom. We were unable to assign the specific regioisomers and conformational isomers of each product present due to similarities in the calculated spectra. It is likely that multiple regioisomers of each product are present in the matrix and the potential energy diagram of the reaction mechanism shows multiple paths to some products. Furthermore, n-butyl group may have some effect on the formation of some regioisomers by altering the charge distribution of ring carbons in n-butyl cp₂Fe. A reaction of O₃ with a ferrocene that has a substituent group that strongly affects charge distribution, such as an amine group, merits further investigation. Lastly, the green matrix formed during the initial dark deposition of O₃ with n-butyl cp₂Fe due to the formation of an n-butyl cp₂Fe-O₃ charge transfer complex.

Acknowledgments

The authors wish to thank Roger Kugel and Anna Gudmundsdottir for helpful discussions. The authors also gratefully acknowledge support of this research by the National Science Foundation under Grant CHE 1110026.

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