Vibrational Overtone Spectroscopy of Butadiene Iron Tricarbonyl and 1,3-Butadiene

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The photoacoustic vibrational overtone spectrum of gaseous butadiene iron tricarbonyl (BDIT) at the third overtone region was recorded and compared to that of 1,3-butadiene. The effect of the metal, determined by an interpretation of the overtone spectrum of the complex, is to lengthen the terminal trans CH bond of the 1,3-butadiene ligand by 0.0024 Å while the terminal cis bond does not change significantly. The assignments of the terminal cis, terminal trans, and nonterminal CH stretch overtone absorptions are supported by ab initio geometry optimization calculations of the trans and cis butadiene and the BDIT complex. The spectrum of the complex possessed three additional bands not seen in the free ligand. These bands originate from vibrational coupling induced by the presence of the metal.

Introduction

Organometallic complexes are known for their catalytic activity in many chemical processes.[1,2] The changes in the ligand properties during coordination, which account for the catalytic activity, have been studied by IR and near-IR spectroscopy.[3] Changes in the infrared spectrum must be analyzed in the normal mode interpretation requiring a normal coordinate analysis and complete vibrational assignments for the ligand and complex. Often these assignments are not available. In this work we demonstrate the usefulness of vibrational overtone spectroscopy for tracking the effects of complexation on specific bonds between a π-bonding organic ligand, butadiene, and its complexed form in butadiene iron tricarbonyl (BDIT). The high vibrational overtone spectrum of the ligands distinguishes different types of olefinic CH stretch absorptions. Shifts in the absorptions or the observation of new peaks report on the changes that have occurred in the ligand during complexation.

Butadiene is the simplest case of π-system resonance with a central bond length shorter than typical single bond lengths.[4] Ab initio calculations indicate that the short central bond of 1.463 Å arises from the sp^2 hybridization with resonance effects stabilizing the planar trans and cis forms.[5] Furthermore, the second most stable conformer is not the planar cis form but the molecule with a torsional angle of 140° from the trans conformer and a longer CC bond (1.474 Å). This structure relaxes the nonbonded hydrogen repulsions that occur in the planar cis form. There are three different calculated CH bond lengths for the trans form (1.071 Å for terminal trans to central CC bond, CH_{tt}; 1.073 Å for terminal cis-to-central CC bond, CH_{tc}; 1.074 Å for nonterminal bond, CH_{nt}), two of which remain unchanged in the 140° form. The CH bonds which interact (cis-cis) shorten by 0.001 Å.[5]

Since individual peaks are observed for each nonequivalent CH bond in the molecule, local mode vibrational overtone spectra yield direct information on the CH bond lengths. The third, fourth, fifth, and sixth overtone transitions in the vibrational overtone spectrum of 1,3-butadiene display three local mode[6] absorption peaks corresponding to the trans structure discussed above.[7] The lowest frequency peak belongs to the longest CH bond, the nonterminal CH, with the other peaks corresponding to the successively shorter bonds. This pattern repeats itself at each overtone level. The anharmonicities for these progressions are similar.[7] Although all three peaks are strong, the absorption for the shortest bond is approximately twice as intense as the peak for the longest bond. These assignments are confirmed by the extensive experimental and theoretical work of Henry and co-workers[8] who find the anharmonicities for the different oscillators of 1,3-butadiene to vary slightly within their experimental error.

Iron tricarbonyl forms stable complexes with conjugated dienes.[9] The molecular orbital diagram for the carbonyl fragment possesses three filled low-lying orbitals with three hybridized high-energy orbitals (e and a_1 symmetry) each with an electron pair. The orbital diagram of butadiene possesses two π-orbitals (one bonding and one antibonding) that interact with the iron carbonyl fragment as acceptors and donors of the electrons.[9] In complexes such as these the interaction of the metal with the π-orbitals in the ligand stabilizes the conjugated system and equalizes the CC bond lengths.[10] The X-ray ligand geometry is planar cis,[11] a form not accessible to experimental study in its free form. The crystalline *Pnma* structure possesses CC bond lengths of 1.46 and 1.45 Å and places the terminal carbons and two of the carbonyl carbons at the base of a square pyramidal structure.

Although the hydrogens were not placed in the X-ray structure of the complex, conclusions can be drawn about their chemical environment. First, because the CC bond lengths are equal, the CC double bonds are longer in the complex than in the free ligand. The CH bond lengths should also be longer in the complex. Second, because of the nonbonded repulsion, the CH bonds in the terminal cis position will be shorter than those in the terminal trans position. The nonterminal CH bonds are influenced by both the lengthening of the terminal CC bonds and the shortening of the CC central bond. In part these ideas are verified by the infrared spectra where the CH stretches of neat liquid BDIT shift 42−65 cm^{-1} to the red compared to the corresponding transitions for 1,3-butadiene.[12,13] In addition, two peaks assigned to the CC stretch (1477 and 1439 cm^{-1}) shifted from 1638 and 1599 cm^{-1} in butadiene.[13]

This paper addresses the possibility that the local mode vibrational overtone spectrum of organic ligands in metal complexes may be used to determine the CH bond length changes of the complex compared to the free ligand. A few reports of vibrational overtone spectra of organometallics have been published.[14,15] Comparisons of the spectra of cyclopentadiene, ferrocene, ruthenocene, and related compounds in the

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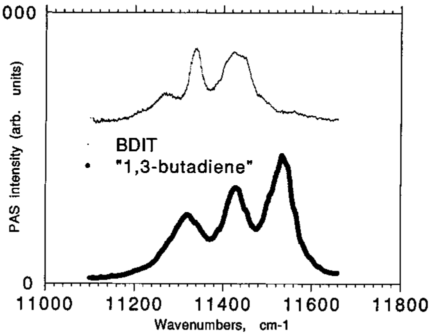

Figure 1. Vibrational spectrum of 1,3-butadiene (room temperature) and butadiene iron tricarbonyl (BDIT) (120 °C) at the third overtone region.

third overtone region indicated that vibrational coupling in the complex splits the peak attributed to the CH olefinic stretch in cyclopentadiene into four peaks.[16] Presented here is the interpretation of the third CH stretch vibrational overtone of 1,3-butadiene iron tricarbonyl. From the discussion above the CH bonds are expected to lengthen, shifting all the overtone CH stretch peaks to the red. In addition the repulsion of the terminal cis CH bonds should shorten these bonds relative to CH bonds in typical alkanes, shifting the terminal cis overtone absorption to the blue.

Experiment

The gaseous overtone spectra of organometallic complexes were obtained by using intracavity laser photoacoustic spectroscopy. The sample was vacuum-transferred into a 20 cm by 1.5 cm photoacoustic cell equipped with a 1751XA^{II} Qualitone microphone and Brewster's angle quartz windows. To increase the signal-to-noise ratio, argon was added to the photoacoustic cell to obtain a total pressure of approximately 500 Torr. A specially designed intracavity oven heated the sample up to 120 °C. The temperature was controlled by the Omega Engineering, Inc. iron constantan thermocouple.

A Spectra-Physics Series 2000 argon ion laser pumped a Spectra-Physics Model 3900S CW Ti:sapphire laser outfitted with a three-plate birefringent filter (2 cm^{-1} bandwidth). An Oriel Motor Mike 18007 control unit controlled the birefringent filter rotation. A McPherson Model 270 0.35 m scanning monochromator with a McPherson Model 789A scan control was used to measure the initial and final wavelengths of the scanning region. The positions of the peaks were corrected using a calibration procedure. Because the resolution of the monochromator is 0.3 cm^{-1}, the measurements were limited by the 2 cm^{-1} resolution of the birefringent filter.

The PTI Model 03-OC4000 optical chopper chopped the argon laser beam at 250 Hz, providing the reference signal for an EG&G Brookdeal Electronics Model 5207 lock-in amplifier. An IBM computer controlled the wavelength scan while recording the photoacoustic signal.

Results and Discussion

The vibrational overtone spectra of 1,3-butadiene and BDIT at the third overtone region are shown in Figure 1. The transition wavenumbers of the peaks are listed in Table 1. The peaks for the 1,3-butadiene spectrum have been previously assigned[7,8] as those belonging to the terminal trans (11 558 cm^{-1}), the terminal cis (11 448 cm^{-1}), and the nonterminal (11 342 cm^{-1}) CH bonds. The metal complex spectrum possesses three main vibrational features. The highest energy absorption appears broadened, indicating that two peaks overlap at this energy. In addition, shoulders of the highest and the lowest energy peaks bring the total to six absorption bands. These six peak transition wavenumbers are tabulated in Table 1.

TABLE 1: Peak Positions and Vibrational Assignments for BDIT and 1,3-Butadiene

peak Positions, cm^{-1}	intensity[a]	assignments
	1,3-Butadiene	
11 333	m	$4v\text{CH}_{\text{nt}}$
11 448	s	$4v\text{CH}_{\text{tc}}$
11 547	s	$4v\text{CH}_{\text{tt}}$
	Butadiene Iron Tricarbonyl	
11 219	vw	combination
11 282	w	combination
11 355	s	combination
11 441	s	$4v\text{CH}_{\text{tc}}$
11 461	s	$4v\text{CH}_{\text{tt}}$
11 504	w	$4v\text{CH}_{\text{nt}}$

[a] vw, very weak; w, weak; m, medium; s, strong.

TABLE 2: Ab Initio CH Bond Lengths (Å) for 1,3-Butadiene

basis sets	STO-3G	3-21G*	6-31G*	6-311G**
trans nonterminal	1.0845	1.0757	1.0782	1.0786
terminal cis	1.0817	1.0744	1.0767	1.0772
terminal trans	1.0812	1.0724	1.0748	1.0753
cis nonterminal	1.0844	1.0759	1.0787	1.0792
terminal cis	1.0809	1.0735	1.0757	1.0764
terminal trans	1.0812	1.0729	1.0752	1.0752

When butadiene complexes to the Fe(CO)$_3$ fragment, the largest geometric change that it undergoes is a rotation around the central bond from trans to cis conformation. Because this change affects the vibrational overtone spectrum, an evaluation of the spectral changes of complexation must be divided into two parts. First, the trans-to-cis isomerization must be accounted for, and second, the bonding of the cis form to the metal must be evaluated.

In previous ab initio calculations[5] on butadiene the nonterminal CH bond lengths do not change with rotation into the 140° stable conformer or the 180° planar cis geometry. We undertook our own ab initio geometry optimization calculations implemented by Spartan of Waveform Inc. The bond lengths resulting from four different basis sets for the trans and cis conformers are listed in Table 2. The optimized geometry for the cis form (140° torsion angle) indicates that the nonterminal CH bond either lengthens or remains the same (STO-3G). The terminal cis CH bond shortens with rotation and the terminal trans CH bond lengthens, making the two terminal CH bonds closer in length.

A correlation exists between the local mode vibrational overtone transition wavenumber and the bond length of the CH oscillator.[17] Empirical expressions for these linear relationships have been derived for related molecules.[17] For example, the transition wavenumbers for heterocyclic liquid samples were correlated to the microwave CH bond lengths.[18] A similar equation was developed to correlate the ab initio 4-21G CH bond lengths of the halogenated benzenes relative to benzene.[19] The changes in the bond length of the halogenated species were given by

$$r_{\text{final}} = r_{\text{initial}} - \frac{\Delta v}{11v}0.001 \text{ or } \Delta r = \frac{\Delta v}{11v}0.001 \qquad (1)$$

where Δv is the frequency shift and v is the vibrational quantum number and r_{initial} is the bond length in benzene itself. This equation makes it easy to see that an $11v$ shift in the transition wavenumber results from a 0.001 Å change in the bond length.

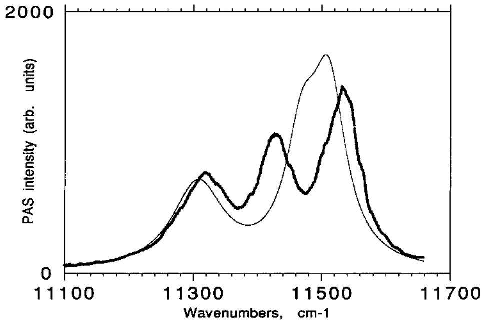

Figure 2. Vibrational spectrum of trans (darker line) and predicted cis (lighter line) conformers of 1,3-butadiene. Cis conformer spectrum was estimated using eq 1.

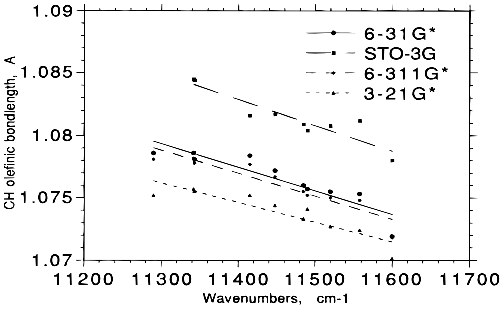

Figure 3. Linear correlations between ab initio CH olefinic bond lengths and transition wavenumbers for 1,3-butadiene and related compounds for different basis sets. Correlation parameters are the following: STO-3G, $r_{CH} = 1.3173-2.06 \times 10^{-5}\nu_{CH}$; 6-31G*, $r_{CH} = 1.2976-1.93 \times 10^{-5}\nu_{CH}$; 6-311G**, $r_{CH} = 1.2887-1.86 \times 10^{-5}\nu_{CH}$; 3-21G*, $r_{CH} = 1.2546-1.58 \times 10^{-5}\nu_{CH}$.

Using this empirical formula, we can predict the appearance of the overtone spectrum of the cis conformer by taking the difference between the ab initio CH bond lengths of cis and trans conformers (see Table 2) and calculating the shift in the spectrum. The 3-21G* basis set was chosen for these predictions because it yielded the best results for the ligand optimization and it was the most sophisticated basis available for the complex geometry optimization described later. The nonterminal CH would shift to the red by 9 cm^{-1}, appearing at 11 324 cm^{-1}. The terminal cis CH would be shifted to the blue by 40 cm^{-1} and appear at 11 488 cm^{-1}, while the terminal trans CH would shift 22 cm^{-1} to the red to appear at 11 526 cm^{-1}. These shifts would place the terminal cis and trans CH's only 38 cm^{-1} apart. Figure 2 displays the predicted cis conformer spectrum compared to the experimental trans conformer spectrum.

To achieve more reliable predictions, an empirical formula similar to the one used above was derived specifically for 1,3-butadienes. The geometry of butadiene and related compounds (2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, and propene) was optimized using the Spartan ab initio method. Then the CH olefinic ab initio bond lengths were plotted against the experimental transition wavenumbers obtained by Fang et al.[7] for 1,3-butadiene and the related molecules named above. The results are given in Figure 3. For all basis sets it was possible to obtain a linear correlation between the overtone transition wavenumbers and CH olefinic bond lengths. Now, by use of the correlation specific to the 1,3-butadienes, the third overtone spectrum for the cis conformer could be re-estimated. The 3-21G* empirical formula, given in the caption of Figure 3, predicts a 21 cm^{-1} red shift for the nonterminal CH, while the terminal CH's move closer to each other (CH_{tc} 25 cm^{-1} to the blue and CH_{tt} 47 cm^{-1} to the red). The predicted spectrum shown in Figure 4 is similar to that in Figure 2.

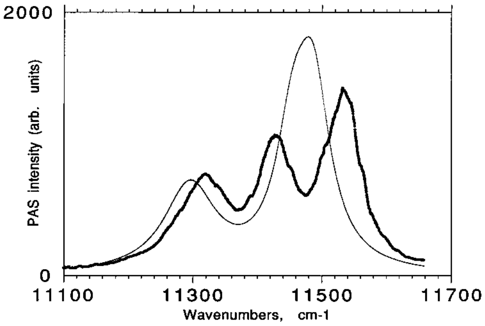

Figure 4. Vibrational spectrum of trans (darker line) and predicted cis (lighter line) conformers of 1,3-butadiene. Cis conformer spectrum was estimated using results of our ab initio calculations.

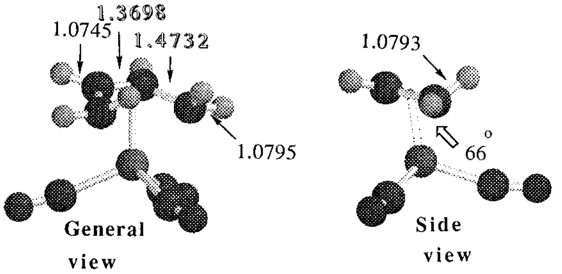

Figure 5. 3-21G* ab initio geometry and bond lengths for butadiene iron tricarbonyl.

With this prediction of the overtone spectrum of the cis form in hand, the next step is to turn to the spectrum of the complex. The above considerations lead to the conclusion that the high-energy broad peak belongs to the terminal CH bonds, which in the complex should possess similar bond lengths. The band at 11 461 cm^{-1} is assigned to CH_{tt} and the band at 11 441 cm^{-1} belongs to CH_{tc}. By use of the 3-21G* empirical formula above, the effect of the metal is to lengthen the terminal trans bond by 0.0024 Å and the terminal cis by 0.0002 Å. This calculated change in the terminal cis bond is not significant. The terminal cis bond does not lengthen as much as the terminal trans because of the nonbonded repulsions in the cis form.

These assignments are supported by our ab initio geometry optimization results (3-21G* basis set) for the butadiene iron tricarbonyl once again implemented in Spartan. The optimized geometry of the complex is shown in Figure 5. The butadiene ligand is not perpendicular to the vertical axis of the molecule. The terminal part of the ligand is moved down making the angle between the plane of the butadiene and the vertical axis of the molecule approximately 66°. In addition, the terminal CH's are twisted to avoid steric interactions with the carbonyl ligand.

These calculations indicate that the terminal CH's lengthen, becoming similar in length in the complex. The nonterminal CH's, whose vibrational overtone transition have yet to be assigned, shorten with the movement of π-density to the nonterminal CC bond. This means that the vibrational overtone transition corresponding to the CH_{nt} should be shifted to the blue compared to the original band in the 1,3-butadiene. Although the use of intensity in assignments is not justified without a full intensity calculation, the transition at 11 355 cm^{-1} is a poor candidate for this assignment because its intensity is too large and its line width is unusually narrow. The band belonging to the CH_{nt} is either hidden under the CH terminal peaks or shifted to even higher energy. It is possible that the high-energy shoulder of the broad peak located at 11 504 cm^{-1} belongs to the third overtone of the CH_{nt} stretch.

This leaves the additional low-energy peaks at 11 219 cm^{-1} and 11 282 cm^{-1} and the narrow intense peak at 11 355 cm^{-1} in the complex spectrum unassigned. Shortening of the CH_{nt}

bond and the lengthening of the CH_{tt} bond can be explained by redistribution of π-electron density in 1,3-butadiene after bonding to the metal. This redistribution may give rise to new modes of vibrational coupling in the ligand. We suggest that the new bands are combinations originating from the coupling of the CH stretches with other vibrational modes of the ligand. It is possible that the new bands are absorptions into states that combine three quanta of one type of CH stretch with one quanta of another type of stretch. In this case the stretch−stretch anharmonicity would need to be unusually large to fit the peaks at 11 219, 11 282, and 11 355 cm^{-1}. It has been proposed[16] that highly energized CH stretching motion primarily interacts with CC stretches and CH bends. If each of three different CH oscillators interacts with one quantum of CC stretch and one CH bend, the three new transitions would fall at 11 278 cm^{-1} ($3\upsilon CH_{nt} + \upsilon C{=}C_{str}(1477) + \upsilon CH_{bend}(1060)$), 11 285 cm^{-1} ($3\upsilon CH_{tc} + \upsilon C{=}C_{str} + \upsilon CH_{bend}$), and 11 361 cm^{-1} ($3\upsilon CH_{tt} + \upsilon C{=}C_{str} + \upsilon CH_{bend}$) in the spectra. The fundamental frequencies used are those from ref 13. Of course, the energy mismatch between the estimated and observed transition wavenumbers could be accounted for by the anharmonicity of stretching and bending motions. Spectra involving a deuterated butadiene ligand would help in the assignment of these combination bands.

Conclusions

The vibrational overtone spectrum of gaseous butadiene iron tricarbonyl was recorded at the third overtone region and compared to the spectrum of 1,3-butadiene. The spectrum of BDIT possessed a more complicated vibrational pattern than the pure ligand spectrum. Transitions due to different types of CH stretches were identified, and three new transitions were observed in the spectrum of the complex. These transitions originate from new channels for vibrational coupling in the ligand opened by the presence of the metal, most likely involving combinations of the CC stretch and CH bend of 1,3-butadiene. The assignments were supported by ab initio geometry optimization for the complex and the free ligand.

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