ammonium hydroxide and oven dried. Samples were photolyzed at 350 ± 30 nm using two Southern New England ultraviolet RPR 3500 bulbs. All EPR measurements were performed with a Varian E-112 spectrometer. The kinetic protocols have been described.[6]

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Registry No. 9-DAF, 832-80-4; CCl_3F, 75-69-4; CF_2BrCF_2Br, 124-73-2; D_2, 7782-39-0; fluorenylidene, 2762-16-5; 9-fluorenyl, 2299-68-5; methylcyclohexane, 108-87-2; toluene, 108-88-3; 2-methyltetrahydrofuran, 96-47-9; ethanol, 64-17-5; propylene glycol, 57-55-6; methylcyclohexane-d_{14}, 10120-28-2; toluene-d_8, 2037-26-5; methylcyclopentane, 96-37-7.

Changes of the Carbonyl Stretching Spectra with Temperature

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Abstract: It is shown that the apparent collapse or coalescence of carbonyl stretching bands of η^4-norbornadiene tricarbonyl iron can be attributed to thermal motion of the carbonyls in *one* potential well. This explanation is in contrast to explanations involving motion between wells. The one-well explanation is also consistent with the expected time scales for all of the possible motions.

I. Introduction

In a number of recent papers, the infrared spectra of the tricarbonyl (η^4-norbornadiene) iron (**1**) has been reported.[1-3] The carbonyl stretching bands appear to broaden and shift together ("collapse"), and at high enough temperature, the collapsed bands appear to narrow. All of this is reminiscent of the behavior of nuclear magnetic resonance (NMR) bands in systems undergoing chemical exchange, and so the infrared spectra are interpreted analogously.

We have, however, argued that vibrational spectra cannot be interpreted in this manner because of the many order of magnitude difference between the magnetic resonance and vibrational time scales.[4-6]

The exchange process for **1** is an internal rotation (Figure 1) in which the three CO groups rotate against the framework formed by the iron and the norbornadiene group. This framework has two symmetry planes, and the axial CO lines up with one of them. The other two CO groups are equatorial and do not line up with a symmetry element of the norbornadiene. A rotation of $2\pi/6$ brings one of the equatorial CO groups to the axial position.

The time scale of the motion required to collapse the bands can be characterized by the splitting between the bands of the interchanging groups, that is about 10 cm^{-1} in the infrared and 10 Hz in the NMR. The infrared splitting corresponds to a time, $t = 2\pi c\bar{\nu}$, for the splitting in wavenumbers (with c the speed of light) of 1.9 ps. The NMR splitting corresponds to a time of $1/2\pi\nu$ or 16 ms. The internal rotation over a barrier is much faster than the NMR time, but slower—or at best the same order of magnitude—than the required infrared time.

η^4-Diene tricarbonyls with low symmetry such as the η^4-butadiene $Fe(CO)_3$ have activation barriers of about 9 kcal/mol and so show no special phenomena in the infrared.[3] In contrast, the η^4-bornadiene and η^4-cyclobutadiene complexes are thought to have barriers of only about 1–1.5 kcal/mol and show collapsing bands in the infrared.[3]

The low barriers make for large torsional displacements of the carbonyl groups, displacements that increase with temperature. These increasing displacements have the effect of moving certain bands in the spectrum toward one another as the temperature increases, and this is just the effect that has been observed. No jump from axial to equatorial need be present.

II. Results and Discussion

A. Band Shifts in the Isotopically Pure Compounds. The exchange of the tricarbonyls occurs by an internal rotation of the carbonyl groups—a motion often described as a turnstile rotation. The effect of the rotation on the spectra can be discussed using our previous treatment[6] of similar effects in the C–H stretching bands of the methyl group at the end of *n*-alkane chains. We follow our previous notation in the following. We start with the isotopically pure tricarbonyls (that is, $X(C^{12}O^{16})_3$) and write the carbonyl Hamiltonian as

$$H_v = \tfrac{1}{2}\sum_{i=1}^{3} G^{-1}\dot{r}_i^2 + \tfrac{1}{2}\sum_{i=1}^{3} Fr_i^2 + \tfrac{1}{2}\sum_{i}^{3}\sum_{j}^{3} fr_ir_j \qquad (1)$$

The r_i are the C═O stretching coordinates, F is the diagonal force constant, and f is the off-diagonal force constant. The kinetic energy matrix element, G^{-1}, is given by $\mu_c + \mu_0$. μ_A is the reciprocal of the mass of the A atom. This vibrational Hamiltonian is for three identical carbonyls—we add the effect of the diene framework separately. The vibrational Hamiltonian is not quite complete, since coupling to the other degrees of freedom is not included. Possible force fields for C–O stretches have been much discussed,[7,8] and better approximations are available if necessary.

We add the interaction with the diene framework with a Hamiltonian

$$H_{VT} = \tfrac{1}{2}\sum_{n=1}^{\infty}\sum_{i=1}^{3} \delta_n \cos\left\{n\left(\theta + (i-1)\frac{2\pi}{3}\right)\right\}r_i^2 \qquad (2)$$

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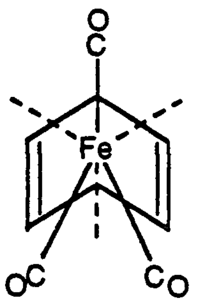

Figure 1. A schematic diagram of η^4-norbornadiene tricarbonyl iron, showing the relation of the position of the carbonyls to the position of the diene. Not all the diene is shown. The dashed lines show an alternate position of the tricarbonyl. The vertical positions (either up or down on the figure) are axial and the other positions are equatorial.

where θ is the angle for internal rotation, and the torsional Hamiltonian is

$$H_T = \tfrac{1}{2}I\dot{\theta}^2 + \tfrac{1}{2}V_m(1 - \cos m\theta) \qquad (3)$$

The various molecules have different values of m (and allowed values of n). The alkanes and the butadiene complex have $m = 3$ and all values of n, while the norbornadiene complex has an extra symmetry plane and thus has $m = 6$ and only even values of n.

Transforming to symmetry coordinates in the C–O stretch

$$r^+ = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3) \qquad r_a = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)$$
$$r_b = \frac{1}{\sqrt{2}}(r_2 - r_3) \qquad (4)$$

we have

$$H_v = \tfrac{1}{2}G^{-1}(\dot{r}^{+2} + \dot{r}_a^{\,2} + \dot{r}_b^{\,2}) + \tfrac{1}{2}(F + 2f)r^{+2} + \tfrac{1}{2}(F - f)(r_a^{\,2} + r_b^{\,2}) \qquad (5)$$

with r^+ the symmetric coordinate and (r_a, r_b) the asymmetric coordinates.

The static and dynamic effects of the diene on the carbonyls can be divided into two parts: a set of average effects that result in shifts and a set of fluctuation effects that result in contributions to the line widths. To make this separation, we write

$$H_1 = H_{VT} - \bar{H}_{VT} \qquad (6)$$

where H_1 is a time-dependent perturbation and $\bar{H}_{VT}$ is the average—both thermal and quantum mechanical—of H_{VT}. To proceed further, we substitute the coordinate transformation eq 4 into H_{VT}.

It is the splittings and collapse of the r_a and r_b bands that are of interest. The r^+ band is separated from this pair by about 70 cm^{-1} and we therefore drop all terms in $\bar{H}_{VT}$ involving r^+. We obtain a long expression involving cos $n\theta$ and sin $n\theta$.[9] The averages over sin $n\theta$ all vanish because the torsional Hamiltonian 3 is even in θ. We finally obtain

$$H_V + \bar{H}_{VT} = \tfrac{1}{2}G^{-1}(\dot{r}_a^{\,2} + \dot{r}_b^{\,2}) + \tfrac{1}{2}(F - f)(r_a^{\,2} + r_b^{\,2}) + \tfrac{1}{2}\sum_n \{\delta_{3n}[\overline{\cos 3n\theta}](r_a^{\,2} + r_b^{\,2}) + \tfrac{1}{4}[\delta_{3n-2}[\overline{\cos (3n - 2)\theta}] + \delta_{3n-1}[\overline{\cos (3n - 1)\theta}](r_a^{\,2} - r_b^{\,2})]\} \qquad (7)$$

where we have redefined the index, n.

The splitting $\omega_a - \omega_b$ is given by

$$\omega_a - \omega_b = \frac{\omega_0}{2(F - f)} \sum_n [\delta_{3n-1}[\overline{\cos (3n - 1)\theta}] + \delta_{3n-2}[\overline{\cos (3n - 2)\theta}]] \qquad (8)$$

and *is temperature dependent because* $\overline{\cos n\theta}$ *is*. Here $\omega_0 = K[G/(F - f)]^{1/2}$ and K is a constant.

To arrive at numerical estimates, we simplify further. We approximate cos $n\theta$ by $(1 - n^2/2)\theta^2$ in eq 7 and 8. This, of course, is a small-angle approximation, but it gives reasonable values for cases we have previously analyzed[6] and the approximation does *not* change the qualitative argument. The reduced mass for the internal rotation is about 272 amu·Å^2.[10] This values gives a rotational constant B of 0.062 cm^{-1}. Using a barrier to rotation of 1.5 kcal/mol for a 6-fold barrier, we obtain a torsional frequency, ν_t, of 22.7 cm^{-1}. The values of the averages are then evaluated as

$$\overline{\cos n\theta} = (1 - n^2/2)\overline{\theta^2}$$
$$\overline{\theta^2} = B/\nu_t \coth \alpha,\ \alpha = hc\nu_t/kT \qquad (9)$$

with h as Planck's constant, k as Boltzmann's constant, and T as temperature.

To simplify still further, we assume that only one of the terms δ_n cos $n\theta$ significant (more can be added as needed). The symmetry restricts us to even numbers and only n's not divisible by three have an effect, so that n is 2, 4, 8, 10, etc. This gives

$$\Delta\omega = \Delta\omega_0 \cos n\theta = \Delta\omega_0((1 - n^2/2)B/\nu_t(\coth (\alpha/2)) \qquad (10)$$

with $\Delta\omega_0$ as the splitting of the a and b bands at zero temperature given by $\delta_n(\omega_0/(2F - f))$, where ω_0 is the frequency of the symmetric mode. Note that for high temperature, that is, $kT \gg h\nu_t$, coth $(\alpha/2) = 2/\alpha$, which is proportional to T. Coth $(\alpha/2)$ is a monotonically decreasing function of α and so the splitting should *decrease* with increasing T, as is observed.

B. Isotope Effects. Recently, the effect of isotopic substitution using C^{13} has been carefully explored.[1] If there is partial isotopic substitution, the vibrational Hamiltonian is changed to

$$H_V + \bar{H}_{VT} = \tfrac{1}{2}[G_1^{-1}r_1^{\,2} + G_2^{-1}r_2^{\,2} + G_3^{-1}r_3^{\,2}] + \tfrac{1}{2}\sum_i [Fr_i^{\,2} + \sum_i \sum_j fr_ir_j] + \bar{H}^{a}_{VT}(r_1^{\,2}) + \bar{H}^{e}_{VT}(r_2^{\,2} + r_3^{\,2}) \qquad (11)$$

Let us consider tricarbonyls with one ^{13}C to be specific.[11] Here there are two distinct Hamiltonians. The first has ^{13}CO in the axial position, that is 1, and G_1^{-1} is the element appropriate for ^{13}CO. G_2^{-1} and G_3^{-1} are then appropriate for ^{12}CO. The other case is for the ^{13}CO equatorial—that is G_3^{-1} is the element for ^{13}CO. Thus, Hamiltonians do not simply factor into normal coordinates, since the combination of the different G matrix elements and the different $\bar{H}_{VT}$ elements for axial and equatorial positions breaks the symmetry. The form of normal coordinates depends on the relative value of the quantity $[G^{-1}(12) - G^{-1}(13)]$ versus the quantity $[\bar{H}^{a}_{VT} - \bar{H}^{e}_{VT}]$. This results in long and not very understandable formulas for the splittings, and so we provide only a qualitative discussion.

A clear example of the collapse of isotope related bands in the carbonyl spectra of **1** is the collapse of the symmetric stretch bands between axial mono ^{13}CO and equatorial mono ^{13}CO on the one hand and between axial mono ^{12}CO and equatorial mono ^{12}CO on the other. As shown in the discussion of the isotopically pure cases (eq 10), increasing temperature decreases the absolute value of $\bar{H}^{a}_{VT} - \bar{H}^{e}_{VT}$. In the limit that $\bar{H}^{a}_{VT} - \bar{H}^{e}_{VT}$ is zero, we can solve the Hamiltonian, eq 11.

The important point is that *in this limit* there is only *one* Hamiltonian for the mono ^{13}CO compound. That is, we can take G_1^{-1} to be for the ^{13}CO and solve for the symmetric stretch (picking G_2^{-1} to be the ^{13}CO gives the same Hamiltonian). In this limit there is no splitting.

Thus, the isotopic splitting of the symmetric stretch must collapse as temperature is increased in about the same way as the splitting of the isotopically pure compounds. The same is true

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[9] Some of the algebra is omitted. Details may be found in ref 6 and in MacPhail, R. A., Ph.D. Dissertation, University of California, Berkeley, 1981.

[10] The moment of inertia of the three carbonyls rotating around their symmetry axis is about 544 amu·Å^2. We divide by two to give an approximate reduced moment of inertia, which takes into account the rotation of the diene.

[11] The treatment here differs from that in ref 6 since here the isotope splitting is about the same magnitude as the splittings due to H_{VT}. Note that G^{-1} might not be simply $\mu_c + \mu_0$, but rather an effective value which takes into account the bonding to the metal atom (ref 7).

for the other pairs of bands that are observed to coalesce.

C. Band Widths, Intermolecular Effects, and Other Considerations. There remains a time-dependent perturbation, the H_1 of eq 6. The effect of this perturbation on the bands can be calculated approximately using the Redfield theory.[6] The theory requires the time correlation functions of the H_1, and in simple cases it gives the widths as a mean-squared amplitude of H_1 times a correlation time τ_c. It is this time that enters into the calculation. τ_c is on the order of 1 to 100 ps and is mostly an intrawell time rather than a time for motion between wells.[6,5] In general, the theory predicts that most simple bands will broaden as the temperature increases, although, as in NMR, it is possible for bands to narrow as the temperature increases. The time τ_c can be very short (picoseconds), corresponding to very fast rates. However, these rates are for intrawell relaxation and, for this type of process, such a short time is thought to be the correct order of magnitude.

In comparing our results to the experiments, it is important to remember that a solid matrix can contribute to the static splittings. A liquid solvent and a solid matrix can each contribute to the width. The time dependence of fluctuations of the solvent will vary with temperature. The effects of the matrix on the spectrum have been illustrated in the equations of ref 6 and evaluated to some extent.

When bands coalesce to form just one band and then apparently narrow as the temperature increases, as observed[1] for the spectrum of isotopically pure **1**, it is difficult to separate the effect of a continuing diminution of the splitting from the effect of the changing width of each component.

III. Conclusions

We have presented a model to account for the observed collapse of the carbonyl stretching bands of **1** and similar compounds. The collapse is due to the increasing amplitude of torsion of the carbonyl groups as the temperature increases. The motion of each carbonyl is almost entirely in its own well and therefore the rate of reaction or change of conformation does not enter our description. There are two types of coalescing bands observed. In the first the bands are split by interaction of the carbonyl groups with the framework. In the second, there is both an isotopic and an interaction effect. The collapse of both types is accounted for. An important point is that the change of the vibrational Hamiltonian from case to case is essentially determined by symmetry arguments. The tricarbonyls may rotate from potential well to well, but our theory does not require an extremely rapid rate of motion. If extreme rates do occur, an occurrence we think unlikely, they would contribute to the observed band collapse in addition to the one-well mechanism.[5]

More information could in principle be obtained from ab initio calculations of the vibrations of **1** as a function of torsional angle.[12] We expect such calculations to show that the stretching frequencies change steeply over the range of motion of one well in a manner consistent with our interpretation of the experimental results. It is possible that the solvent or matrix effects will have to be separated from the intramolecular effects to make this comparison quantitative. The referee suggested a further possibility—that the changes in the bending bands, which will qualitatively follow those of the stretches, will, with the help of the ab initio calculations, distinguish between the mechanisms for the exchange of the carbonyls.

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An Investigation of the Homolytic Dissociation of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ and Related Complexes. The Role of Ligand Substitution on the Solution Thermochemistry of Metal–Metal Bond Cleavage

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Abstract: Thermodynamic parameters for dissociation of the metal–metal bonded dimers $[\eta^5\text{-}C_5R_5Cr(CO)_2(L)]_2$ (R = H, L = CO, P(OMe)$_3$; R = Me, L = CO) have been studied by several techniques including variable-temperature FTIR spectroscopy, magnetic susceptibility, NMR spectroscopy, and solution calorimetry. Values for the Cr–Cr bond strength are in the range 11–15 kcal/mol. Results obtained via NMR techniques in this system disagree with all other results probably due to a multiplicity of populated states for the radical monomers. For the radicals $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PR_3)\}$ (R = Ph, Et), no sign of dimer formation is found even at −80 °C, indicating that the Cr–Cr bond strength is <8 kcal/mol for these compounds. Calorimetric measurements of the heats of reaction of Hg and $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ forming $Hg[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ have been measured for R = H, Me and indicate average Hg–Cr bond strengths of 20.3 and 20.7 kcal/mol, respectively. Synthetic and spectroscopic details are described for $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ as well as its structure as determined by X-ray crystallography. The Cr–Cr distance, 3.3107 (7) Å, is longer than that reported for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$; however, the increased tendency to form radicals for this complex is due more to entropic than enthalpic factors.

Introduction

In spite of the importance of metal–metal bonded complexes in organometallic chemistry, there are relatively few reliable metal–metal bond dissociation energies available for complexes in solution. There are several techniques available for obtaining metal–metal bond strength estimates. These are illustrated by the well-studied complex manganese carbonyl:

$$Mn_2(CO)_{10} \rightarrow 2\{Mn(CO)_5\} \qquad (1)$$

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