

Dynamic IR Spectroscopy: Occurrence and Predictability of Coalescence in the CO Stretching Vibrations of ^{13}CO -Enriched Tricarbonyl(η^4 -norbornadiene)iron^{II}

James J. Turner,^{*,†} Friedrich-Wilhelm Grevels,^{*,‡} Steven M. Howdle,[†] Jürgen Jacke,[†] Mark T. Haward,[†] and Werner E. Klotzbücher[†]

Contribution from the Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England, and Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34-36, D-4330 Mülheim a. d. Ruhr, Germany. Received May 1, 1991. Revised Manuscript Received July 1, 1991

Abstract: The $\nu(\text{CO})$ IR spectra of ^{13}CO -enriched $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ (**1**) has been recorded in noble gas solvents as a function of temperature. As the temperature is raised (from -146 °C to $+88$ °C) several of the bands broaden, coalesce, and collapse in a manner similar to that observed in the variable-temperature NMR spectra of fluxional molecules. At the lowest temperature the complex band pattern can be accurately fitted using the energy factored CO force field. By appropriately averaging the force field parameters, the spectrum at high temperature can be accurately predicted. These observations are interpreted in terms of a very fast CO site exchange process in the organometallic complex.

Introduction

The application of NMR spectroscopy to the study of dynamic processes is well known.¹ As the rate of a site exchange process increases with temperature, the NMR signals may broaden, coalesce, and ultimately collapse into fewer peaks. In principle similar effects should be observable in vibrational spectroscopy provided the underlying dynamic processes occur with rate constants much larger than those required for NMR band collapse.² Recall that in consequence of the uncertainty relation ($\Delta E \times \Delta t \geq h/2\pi$), the coalescence of spectral features separated in frequency by $\Delta\nu$ involves rate constants ($k = 1/\tau$, the reciprocal of the lifetime in a particular structure) of the order of $2\pi \times \Delta\nu$. Thus to bring about coalescence of two IR bands separated by, for example, 5 cm^{-1} requires an *ultrafast* exchange process with $k > 10^{12} \text{ s}^{-1}$ ($\tau < 10^{-12} \text{ s}$). This may be compared with dynamic NMR spectroscopy, which typically involves chemical shift differences up to several hundred hertz and, consequently, exchange rate constants not necessarily exceeding $10^3 - 10^4 \text{ s}^{-1}$.

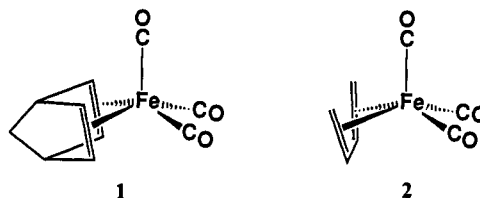
In NMR spectroscopy it is possible, using modified Bloch equations for the simulation and analysis of the line shapes, to obtain the rate constants as a function of temperature, and hence to evaluate the activation energy of the process responsible for the spectral changes.

In vibrational spectroscopy there have been a variety of experiments purporting to illustrate broadening and even collapse of bands and in some cases to extract kinetic data and to determine activation parameters of low-barrier processes.³ However, doubts have been expressed about the viability of such interpretations,^{2,3} in particular the use of the (appropriately modified) Bloch equations.

There have been counter arguments, for instance,⁴ that the Bloch equation approach is valid provided the energy barrier is higher than $2kT$. We plan to discuss elsewhere the details of such arguments, but a critical question seems to be whether the range of chemical exchange can be varied on the IR time scale from very slow to very fast ("frozen" to "rapid"), i.e., from well-separated vibrational bands to a collapsed spectrum. In this paper, which builds on preliminary reports,⁵ we describe what we believe is the first clear example of such a system.

Results and Discussion

Infrared Spectrum of $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ (1**).** In two recent communications⁵ the Mülheim group described dramatic



temperature effects on the infrared spectra of $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$ complexes (diene = norbornadiene, 1,5-cyclooctadiene) in hydrocarbon solutions, which provide striking evidence of CO stretching vibrational band coalescence upon warming from -140 °C to room temperature. Considering the symmetry (C_3) of such compounds (see **1** for the norbornadiene complex), one should expect three IR-active CO stretching vibrations (a' , a' , and a''), which are indeed observed at low temperature. However, as the temperature is raised, the low-frequency pair of bands (a' and a'') appear to broaden, coalesce, and eventually collapse at ca. -10 °C to a single band; meanwhile, the high-frequency (a') band is only marginally affected. Similar observations were made with $\text{Fe}(\text{CO})_3(\eta^4\text{-cyclobutadiene})$, but here the coalescence of the low-frequency pair of bands occurs at -80 °C.⁶ These spectral changes have been interpreted^{5,7} in terms of a very rapid CO site exchange process which renders the three CO groups vibrationally equivalent, i.e., imposes (pseudo)- C_{3v} symmetry on the complexes, such that the low-frequency a' and a'' CO stretching vibrations become degenerate. The details of the exchange mechanism are unknown, but this does not affect the argument.⁸ It seems likely that a cyclic permutation based on a turnstile mechanism is operative, as illustrated in Figure 1.

Careful monitoring of temperature-dependent, subtle changes in band positions and shapes is indispensable for confirming the

(1) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(2) Wood, K. A.; Strauss, H. L. *J. Phys. Chem.* **1990**, *94*, 5677.

(3) Reviewed in: Wood, K. A.; Strauss, H. L. *Int. Rev. Phys. Chem.*, in press.

(4) Viot, P.; Tarjus, G.; Borgis, D.; Bratos, S. *J. Chem. Phys.* **1989**, *90*, 7022.

(5) Grevels, F.-W.; Jacke, J.; Klotzbücher, W. E.; Krüger, C.; Seevogel, K.; Tsay, Y.-H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 885. Grevels, F.-W.; Jacke, J.; Seevogel, K. *J. Mol. Struct.* **1988**, *174*, 107.

(6) Jacke, J. Ph.D. Dissertation, Max-Planck-Institut für Strahlenchemie/Universität-Gesamthochschule Duisburg, 1989.

(7) Changes with temperature in the $\nu(\text{CO})$ IR band pattern of $\text{Os}_4(\text{CO})_{14}$ have also been interpreted in terms of carbonyl exchange on the IR time scale: Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1988**, *7*, 1867.

(8) Wang, P.; Agrafiotis, D. K.; Streitwieser, A.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 201.

[†] Dedicated to Professor Kurt Schaffner on the occasion of his 60th birthday.

[†] University of Nottingham.

[‡] Max-Planck-Institut für Strahlenchemie.

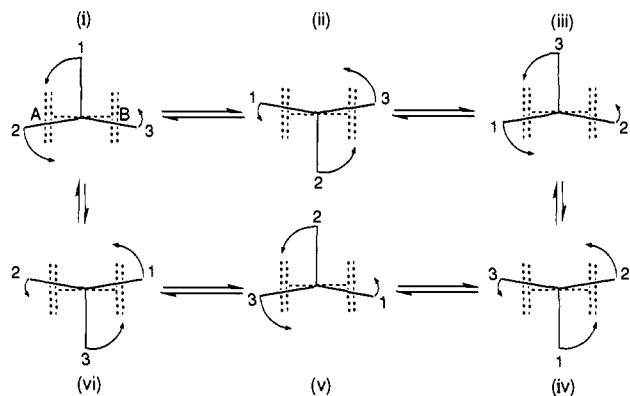


Figure 1. Schematic representation of possible exchange process based on turnstile mechanism which will exchange the CO groups of $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ (**1**). The molecule is viewed along an axis lying in the symmetry plane; the dotted lines represent the diene. In the motion that converts i to ii, group 1 moves from the axial to the equatorial position and group 2 from the equatorial to the axial position, but group 3 merely adjusts from one equatorial position to another. Note that, because this diene has a plane of symmetry (labeled AB in i), all six configurations have the same energy, and configurations i and iv, ii and v, iii and vi are identical. Of course, if there is no change in internal angular momentum, the diene group will actually rotate in the opposite direction to the direction of motion of the CO groups.

above interpretation and for deepening our understanding of the proposed exchange process. Liquid noble gases (LNG) are the solvents of choice for such a thorough investigation. They have proved to be extremely useful solvents for both spectroscopic studies⁹ and for the characterization of photochemically generated intermediates.¹⁰ Both liquid krypton (LKr) and liquid xenon (LXe) (or mixtures of them, LKr/Xe) provide a low-temperature environment in which band broadening due to solvent is at a minimum and hence IR bands tend to be very sharp. Moreover, the absence of any solvent absorptions is very helpful for accurately studying band profiles. Liquid xenon becomes supercritical (scXe) at 16.9 °C and 59 atm pressure and provides an environment for unusual chemistry;¹¹ in the present context scXe as a high-temperature solvent should have less solvent perturbation than most other solvents and provide a more direct comparison with low-temperature LNG spectra.

One crucial point is to separate general temperature-dependent band shifts and changes in profile from those effects originating from the exchange process. Thus, as a reference point for our studies on $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ (**1**), we first consider the spectrum of $\text{Fe}(\text{CO})_3(\eta^4\text{-butadiene})$ (**2**), which demonstrates no unusual temperature effects and serves as a calibrant molecule. Variable-temperature NMR studies¹² have shown that the activation barrier for CO site exchange in **2** is approximately 9 kcal mol⁻¹, with a rate constant at ambient temperature of ca. 10⁶ s⁻¹. From the Introduction it is clear that this is far too slow to have any observable effect on the vibrational spectrum. Consequently, the structure of **2** can be considered to be static on the IR time scale, in accordance with its IR spectra in hydrocarbon solvents.⁵ Figure 2a shows the $\nu(\text{CO})$ region of the IR spectrum of **2** in liquid krypton doped with approximately 10% of xenon (LKr/Xe). The spectrum shows three bands at 2059.7, 1994.0, and 1983.2 cm⁻¹, readily assigned^{6,13,14} with the assistance of ¹³CO substitution to

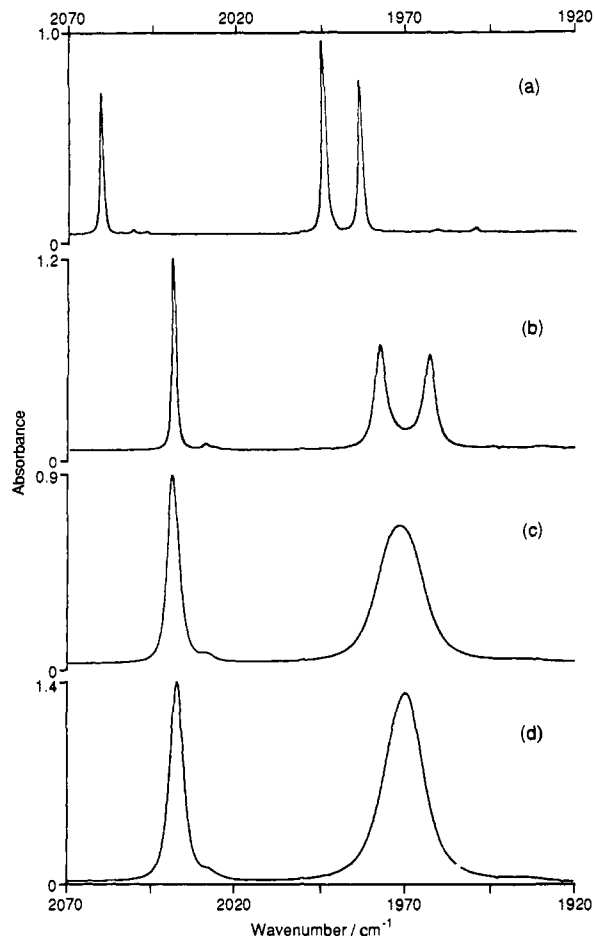


Figure 2. IR spectra in the $\nu(\text{CO})$ region of (a) $\text{Fe}(\text{CO})_3(\eta^4\text{-butadiene})$ (**2**) in LKr/Xe at -150 °C, (b) $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ (**1**) in LKr/Xe at -150 °C (the weak bands in these spectra are due to ¹³CO groups in natural abundance), (c) **1** in scXe at 25.5 °C, and (d) **1** in scXe at 102 °C. The spectra were recorded (32K data points; Happ-Genzel apodization; ca. 0.5-cm⁻¹ resolution) on a Nicolet 7199 FTIR instrument with MX 3600 data station.

the *a'*, *a'*, and *a''* normal modes of the $\text{M}(\text{CO})_3$ group with C_3 symmetry. The high-frequency *a'* band and the low-frequency pair of bands (*a'* and *a''*) have half-widths (fwhm) of 1.17 and 1.36 cm⁻¹, respectively, which indicate that the solvent has an influence on bandwidth which depends on the particular normal mode.^{15a} However, the effect is small and the spectrum changes little with temperature.^{11a}

Figure 2b shows the $\nu(\text{CO})$ region of the spectrum of **1** under the same conditions. As expected for a molecule with a structure similar to **2**, it exhibits the typical *fac*- $\text{M}(\text{CO})_3$ pattern with three bands of comparable *integrated* intensities. It is striking, however, that, although the high-frequency *a'* $\nu(\text{CO})$ bands for both compounds **1** and **2** have very similar half-widths (1.17 and 1.34 cm⁻¹, respectively), the low-frequency bands of **1** (*a'* and *a''*) are much broader (3.6 cm⁻¹) than those of **2** (1.36 cm⁻¹). This parallels our previous observations in hydrocarbon solvents⁵ (apart from the greater bandwidth in those solvents) and indicates the onset of band broadening even at the lowest accessible temperature.

Figures 2c and 2d show the $\nu(\text{CO})$ pattern of **1** in scXe at 25.5 °C and 102 °C. At 25.5 °C the high-frequency *a'* band is broader (fwhm ca. 4.1 cm⁻¹) than at low temperature in LKr/Xe; since **2** shows a comparable bandwidth^{11a} under the same conditions, this is almost certainly simply a solvent effect. However, the low-frequency pair (*a'* and *a''*) has collapsed to a single, broad band (fwhm = 15.3 cm⁻¹). On warming to 102 °C, the high-frequency band *broadens* slightly (fwhm = 4.6 cm⁻¹), but what

(9) Bulantin, M. O. *J. Mol. Struct.* **1973**, *18*, 51. Kimel'feld, Ya. M. *Russ. Chem. Rev.* **1988**, *57*, 730. Beattie, W. H.; Maier, W. B., II; Holland, R. F.; Freund, S. M.; Stewart, B. *Proc. SPIE (Laser Spectrosc.)* **1978**, *158*, 113.

(10) Turner, J. J.; Poliakoff, M.; Howdle, S. M.; Jackson, S. A.; McLaughlin, J. G. *Discuss. Faraday Soc.* **1988**, *86*, 271. Turner, J. J.; Poliakoff, M.; Healy, M. A. *Pure Appl. Chem.* **1989**, *61*, 787.

(11) (a) Howdle, S. M. Ph.D. Thesis, 1989, University of Nottingham, UK. (b) Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804.

(12) Kruczynski, L.; Takats, J. *J. Am. Chem. Soc.* **1974**, *96*, 932; *Inorg. Chem.* **1976**, *15*, 3140.

(13) Haward, M. T. Unpublished calculations.

(14) Warren, J. D.; Clark, R. *J. Inorg. Chem.* **1970**, *9*, 373.

(15) (a) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975. (b) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

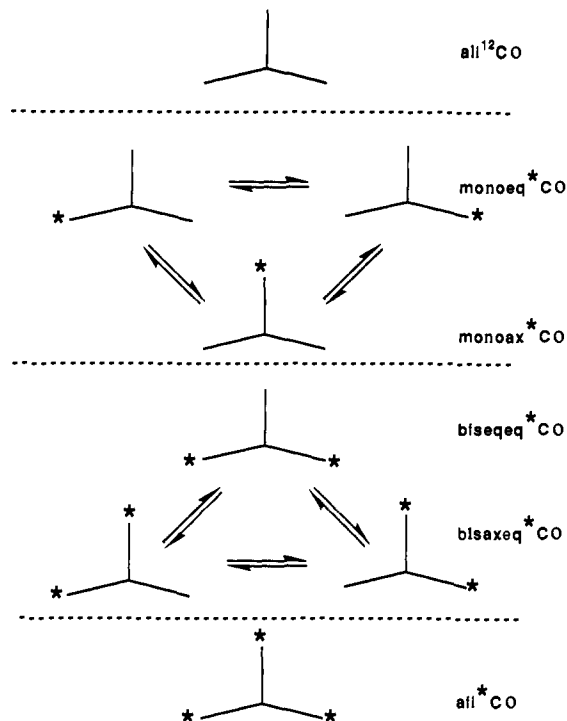


Figure 3. Schematic representation of **1** and its isotopomers with labeled CO group(s) (*) in the various positions: ax = axial, eq = equatorial; thus, for example **monoax*CO** represents the species with a single *CO group in the axial position, the others being ^{12}CO groups. The two **monoax*CO** and the two **bisaxeq*CO** substituted species are equivalent.

is particularly important is that the low-frequency band has narrowed (fwhm = 13.4 cm^{-1}). Since we expect all bands to experience a solvent broadening effect, the observed opposite behavior implies that the low-frequency band narrowing is due to a process which has a larger effect than that of solvent broadening. This kind of band narrowing upon further warming, following the collapse of bands at intermediate temperatures, is fully consistent with the underlying process being a very fast CO site exchange. Unfortunately, the system cannot be further raised in temperature without decomposition of the sample (or leakage of the IR cell), thus preventing further monitoring of this trend.

One might query the proposed dynamic CO site exchange as the (exclusive) origin of the temperature-dependent spectral changes observed for **1** and could invoke other, quite different explanations. These could include mode-sensitive solvent effects, *intra* (rather than *inter*) potential well dynamics,² dephasing, and free rotation above a low-energy barrier. It seems possible that the dynamic exchange is operating in combination with other effects; these possibilities will be discussed in detail elsewhere. However, returning to the comment in the Introduction, if a "rapid" $\nu(\text{CO})$ spectrum can be accurately predicted on the basis of a "frozen" spectrum, other explanations become less persuasive, unless they can also accurately predict such changes. The prediction of "rapid" from "frozen" is actually a more subtle problem than might appear, but before discussing it in detail we shall describe further experiments on **1** which we believe fulfil this requirement of predictability, and also provide further evidence for the occurrence of the dynamic CO site exchange.

^{13}CO -Enriched $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$. (a) **Isotopic Labeling: Underpinning the Exchange.** Partial enrichment of **1** with isotopically labeled carbon monoxide (*CO, e.g., ^{13}CO or C^{18}O) will yield a mixture of the isotopomeric molecules shown schematically in Figure 3. At low temperatures the $\nu(\text{CO})$ spectrum will show the superimposed three-band patterns of each species (note that the two **monoax*CO** and two **bisaxeq*CO** species will have identical spectra; in addition, because of the symmetry, some of the bands of differently substituted species will necessarily overlap; see later). On varying the temperature we cannot expect any new information from the fully labeled complex **all*CO**, since the spectral changes should precisely parallel those of the unlabeled

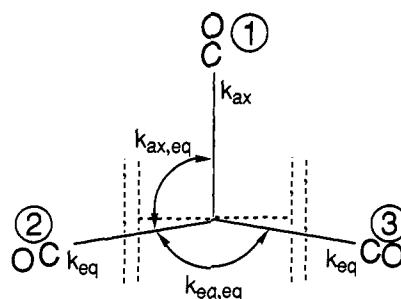


Figure 4. Numbering of CO groups and force field parameters in $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ (**1**); k_{ax} and k_{eq} are principal $\nu(\text{CO})$ stretching force constants, and $k_{\text{ax,eq}}$ and $k_{\text{eq,eq}}$ are interaction force constants.

parent, **all ^{12}CO** , regardless of the nature of the underlying process. However, if an ultrafast CO site exchange is operating, it will interconvert, on the IR time scale, the two sets of positional isotopomers, as shown in Figure 3, with striking effects on the spectra. We expect that, for the two (distinct) mono-substituted species, the two separate three-band patterns will coalesce to a *single* three-band spectrum (note that rapid exchange will still leave a molecule which, because of the one ^{13}CO group, has C_3 symmetry and hence three $\nu(\text{CO})$ bands). Similar behavior is expected for the bis-substituted species. As will be seen shortly, spectral changes are seen which match these predictions, but a proper interpretation requires a knowledge of the energy factored CO force field, which itself requires a knowledge of isotopic frequencies.

(b) **The Energy Factored CO Force Field.** The $\text{Fe}(\text{CO})_3$ group in the static structure of **1** (or **2**) has C_3 symmetry. In the energy factored CO force field,¹⁵ four force constants (k_{ax} , k_{eq} , and $k_{\text{ax,eq}}$, and $k_{\text{eq,eq}}$; Figure 4) are required to describe the CO stretching vibrations. It is not possible to obtain these parameters from the three frequencies shown in Figure 2b, and hence it is necessary to isotopically enrich **1** with either ^{13}CO or C^{18}O . The energy factored CO force field is better obeyed¹⁶ with ^{13}CO substitution than with C^{18}O ; hence the former was used for the isotopic labeling of **1**. Irradiation of **1** in hydrocarbon solution at ambient temperature under ^{13}CO atmosphere results in statistical incorporation of the isotopic label. The sample of $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ used in this study contains an average ^{13}CO enrichment of 42% ($n = 0$, 19%; $n = 1$, 43%; $n = 2$, 31%; $n = 3$, 7%).

Figure 5a shows the $\nu(\text{CO})$ IR spectrum of this sample, recorded in 2-methylpentane at -140°C . Figure 5b shows the spectrum of the same sample obtained under similar conditions to those in Figure 2b, i.e., LKr/Xe at -146°C ; the advantage of using liquid noble gas solvents is clearly demonstrated. Table I lists the frequencies appropriate to Figure 5b. The assignment of bands to the positional isotopomers is greatly helped by the relative intensities, which reflect the percentage enrichment and the statistical weighting referred to above. Based on the experimental data in Table I, the CO force field parameters ($k_{\text{ax}} = 1618.7$, $k_{\text{eq}} = 1595.9$, $k_{\text{ax,eq}} = 34.6$, and $k_{\text{eq,eq}} = 40.8 \text{ N m}^{-1}$) have been calculated using the variable reduced mass technique.^{15,16} The $\nu(\text{CO})$ normal coordinates of the various isotopomeric molecules, expressed in terms of the CO stretching internal coordinates, are also given in Table I and schematically represented in Figure 6. The relative intensities (Table I) are calculated on the basis of these normal coordinates by (a) assuming that the OC-Fe-CO angles are the same as in $\text{Fe}(\text{CO})_3(\eta^4\text{-1,5-cyclooctadiene})$,⁵ (b) assuming that the local dipole moment derivatives $(\partial\mu(\text{CO})_i/\partial r_i)$ are the same for each CO group, and (c) accounting for the relative concentrations of the various isotopomers. The calculated spectrum is shown in Figure 5c.

The frequency fit is extremely good (rms error $<0.2 \text{ cm}^{-1}$), but it is clear that some of the bands are broader than others;¹⁷ for

(16) Burdett, J. K.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Inorg. Chem.* **1978**, *17*, 948.

Table I. Experimental and Calculated Spectra for 42% ^{13}CO -Enriched $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene)}$ in LKr/Xe at $-146\text{ }^\circ\text{C}$ (frequencies in cm^{-1} ; intensities in arbitrary units)

	frequency		intensity calc ^c	label ^d		normal coordinate ^e				
	expt ^a	calc ^b				r_1	r_2	r_3	r_1	r_2
all^{12}CO	2038.0	2037.8	0.751	a	a'	0.640	+	0.543	+	0.543
	1976.3	1976.3	1.306	b	a'	0.769	-	0.452	-	0.452
	1961.9	1962.0	0.941	c	a''			0.707	-	0.707
monoax^{13}CO	2025.6	2025.4	0.607	d	a'	0.393	+	0.650	+	0.650
	1961.9	1962.0	0.682	e	a''			0.707	-	0.707
	1942.7	1942.7	0.849	f	a'	0.920	-	0.278	-	0.278
mono^{13}CO	2028.6	2028.7	1.075	g		0.731	+	0.346	+	0.588
	0	1973.1	1.804	h		0.660	-	0.143	-	0.737
	0	1928.7	1.397	i		0.171	-	0.927	+	0.333
	0	1949.2	0.655	k	a'	0.868	+	0.351	+	0.351
biseq^{13}CO	2018.5	2018.5	0.399	j	a'	0.868	+	0.351	+	0.351
	1917.0	1916.9	0.471	l	a''	0.496	-	0.614	-	0.614
bisax^{13}CO	2011.9	2012.2	0.847	m		0.447	+	0.794	+	0.413
	0	1947.1	1.094	n		0.767	-	0.577	+	0.281
	0	1925.0	1.108	o		0.461	+	0.191	-	0.866
all^{13}CO	1990.7	1990.9	0.272	p	a'	0.640	+	0.543	+	0.543
	0	1930.8	0.473	q	a'	0.769	-	0.452	-	0.452
	1917.0	1916.9	0.341	r	a''			0.707	-	0.707

^a At $-146\text{ }^\circ\text{C}$; zero entries refer to bands for which the frequencies, because of overlap, cannot be accurately measured; they are ignored in the refinement. ^b Force constants $k_{\text{ax}} = 1618.6$ (6), $k_{\text{eq}} = 1595.9$ (3), $k_{\text{ax,eq}} = 34.6$ (3), $k_{\text{eq,eq}} = 40.7$ (8) Nm^{-1} ; reduced mass ratio 0.97698; rms error = 0.16 cm^{-1} . ^c Assuming that the structure is the same as $\text{Fe}(\text{CO})_3(\eta^4\text{-1,5-cyclooctadiene})$. ^d The first column refers to Figures 5 and 6 and the second to the irreducible representations of the vibrations of those molecules which have C_s symmetry. ^e r_1 , r_2 , and r_3 refer to the stretching of the CO groups in positions 1 (ax), 2 (eq), and 3 (eq); see Figure 4. The approximate normal modes are plotted in Figure 6.

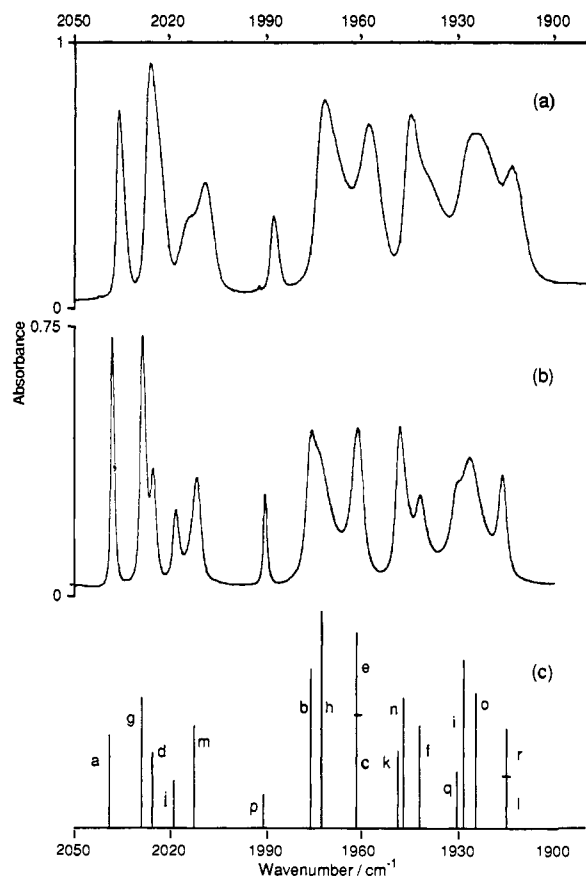


Figure 5. IR spectra in the $\nu(\text{CO})$ region of ^{13}CO -enriched (42%) **1** in (a) 2-methylpentane at $-140.5\text{ }^\circ\text{C}$ (spectra were recorded on a Perkin-Elmer 1760 FTIR instrument with PE 7500 data station giving ca. 0.5-cm^{-1} resolution) and in (b) LKr/Xe at $-146\text{ }^\circ\text{C}$ using Nicolet 730 FTIR instrument, employing 54K data points, Happ-Genzel apodization-digital smoothing, giving a resolution of ca. 0.3 cm^{-1} . (c) Calculated spectrum for ^{13}CO -enriched **1** as described in the text and Table I.

instance, in the high-frequency region, the totally symmetric stretches (a and p in Figure 5c) of the **all ^{12}CO** and **all ^{13}CO**

(17) The fact that the bands differ in half-width is the reason for not attempting to define Lorentzians in the calculated spectrum.

molecules are narrower than the corresponding bands (g, d, j, and m) for the **mono ^{13}CO** and **bis ^{13}CO** molecules.¹⁸ Since broadening of bands implies some shift of frequency, this places a limit on the absolute accuracy of the force field, but we estimate that any error is very small.

(c) **Spectral Changes with Temperature.** Comparison of Figures 7a and 7b demonstrates the effect of raising the temperature by $39\text{ }^\circ\text{C}$ from $-146\text{ }^\circ\text{C}$ to $-107\text{ }^\circ\text{C}$. The first point to note is that the bands a and p are shifted up in frequency by about 2 cm^{-1} but retain almost identical half-widths. Other bands in the spectrum shift somewhat more¹⁹ and show some broadening. For instance, it is clear that the isotopic pairs g/d and j/m are broadening and coalescing. This is a particularly crucial observation since it quantifies the predictions made in section a; the coalescence of these pairs is precisely what is expected if the positional isotopomers **monoax ^{13}CO /mono ^{13}CO** and **bisax ^{13}CO /biseq ^{13}CO** interconvert rapidly on the IR time scale. This is shown schematically in Figure 8. Moreover, the normal modes of d, g, j, and m, like those of a and p, are all in-phase combinations of the internal coordinates, and in view of this similarity it is unlikely that the collapsing has anything to do with mode-sensitive solvent effects. Figures 7c and 7d show the spectrum of the ^{13}CO -enriched sample of **1** in scXe at $25\text{ }^\circ\text{C}$ and at $88\text{ }^\circ\text{C}$. As expected from the behavior of the unlabeled complex (Figure 2), further coalescence/collapse has occurred. Can the changes, and the (nearly) constant positions of band a and p, be predicted from the force field parameters extracted from the low-temperature, nearly "frozen" spectrum?

(d) **Prediction of Spectral Change.** It is instructive to take the NMR analogy first. In NMR spectroscopy it is a straightforward matter to calculate a spectrum in the fast exchange limit if the chemical shifts and coupling constants are known for the "frozen" spectrum. One simply takes the statistically weighted averages of these parameters, the weighting depending on the contribution of the different structures (or in the case of a degenerate rearrangement, the different substructures) to the equilibrium structure. Of course, it is more difficult to predict the appearance of the spectrum at some intermediate stage. Such a simulation

(18) In fact the bands j and m have themselves different half-widths. This may arise because, as the molecule twists slightly from the equilibrium position, the equivalence between the two **bisax ^{13}CO** molecules is removed. Preliminary calculations show that this will split band m, or in practice appear as an additional broadening.

(19) Careful studies on both **1** and **2** show that the solvent shift for the bands derived from the high-frequency in-phase modes (i.e., a, d, g, j, m and p) is approximately half that for the other modes.^{11a}

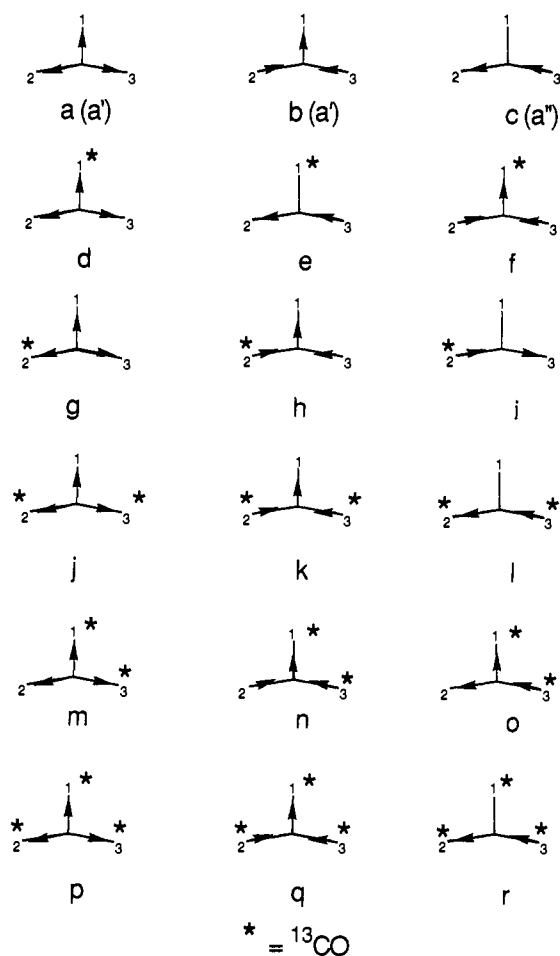


Figure 6. Schematic representation of the approximate $\nu(\text{CO})$ normal modes of complex **1** and isotomers with ^{13}CO group(s) (*) in the various positions. The letters refer to Table I and Figure 5.

commonly involves the computer-assisted application of an appropriate "Dynamic NMR" program based on modified Bloch equations or, for complicated systems with spin-spin coupling, a density matrix treatment.¹ The important point to note is that the data used in describing the NMR spectra, chemical shifts, and coupling constants are frequency quantities, i.e., directly related to the transition energies. Put differently, the effective Hamiltonian is the "spin"-Hamiltonian which is expressed in terms of chemical shifts and coupling constants. Averaging these data in order to predict the spectrum in the fast exchange limit will not change the sum of the transition energies. What is the IR spectroscopic equivalent?

Vibrational spectra are most elegantly treated by the FG matrix formalism. The eigenvalues λ_i are obtained by solving the equation

$$|\mathbf{FG} - \mathbf{E}\lambda| = 0$$

in which the **F** matrix contains force field parameters and the **G** matrix contains geometrical and mass parameters. The important points to note are that the eigenvalues (λ_i) are proportional to the squares of the observable quantities, the frequencies, and that neither the **F** nor **G** matrices are expressed in terms of parameters which are proportional to frequency. Thus there is no equivalent to the spin-Hamiltonian. Hence statistically averaging force constants and geometrical terms is not equivalent to averaging chemical shifts and coupling constants in NMR spectroscopy. However, in the energy factored CO force field, the **G** matrix is diagonal in the reduced mass of the CO groups; thus in obtaining the eigenvalues there is no need to consider averaging the geometry. What about the **F** matrix?

Let us consider the simplest case, a single vibrator, say a CO group, rapidly exchanging (on the IR time scale) between two different environments (a) and (b), for which it has the same

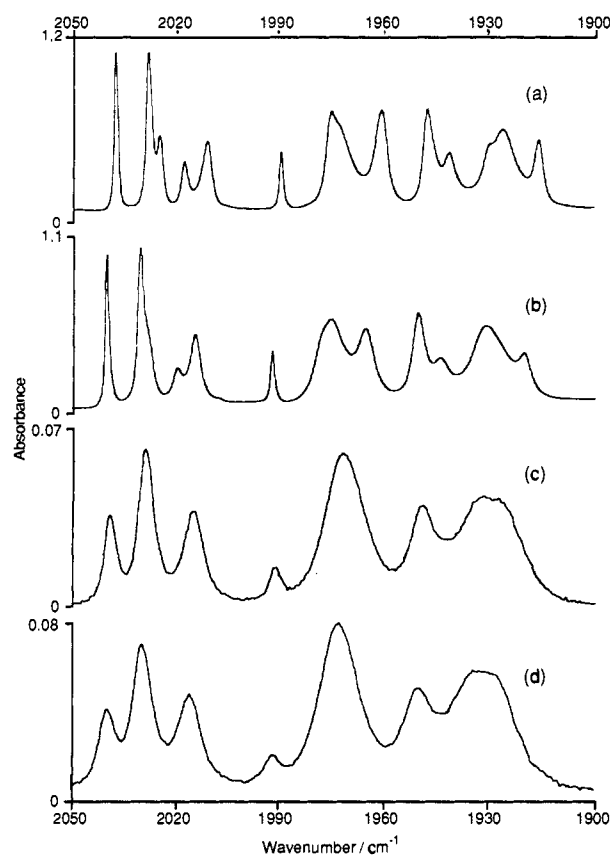


Figure 7. IR spectra in the $\nu(\text{CO})$ region of ^{13}CO -enriched (42%) **1** (a) in LKr/Xe at -146°C (cf. Figure 5b), (b) in LKr/Xe at -107°C , (c) in scXe at 25°C , and (d) in scXe at 88°C .

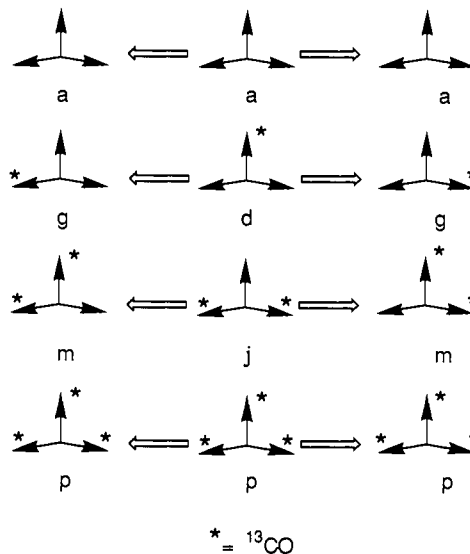


Figure 8. Schematic representation of the CO site exchange process involving the high-frequency in-phase modes of complex **1** and its isotomers.

probabilities but in which it vibrates at different wavenumbers $\bar{\nu}_a = (1/2\pi c)(k_a/\mu_{\text{CO}})^{1/2}$ and $\bar{\nu}_b = (1/2\pi c)(k_b/\mu_{\text{CO}})^{1/2}$. The "frozen" spectrum will exhibit two bands of equal intensity at $\bar{\nu}_a$ and $\bar{\nu}_b$, whereas in the rapid exchange limit we expect to observe a single band at the average wavenumber position, $(\bar{\nu}_a + \bar{\nu}_b)/2$. Obviously, averaging the force constants k_a and k_b does not yield the same result which means that the total vibrational energy would not be kept constant. Fortunately, in the vibrational spectra of metal carbonyl complexes, all the $\nu(\text{CO})$ bands generally occur in a narrow frequency range, which means that in our simplest example in practice there is virtually no difference between av-

Table II. Averaged Spectrum for 42% ¹³CO-Enriched Fe(CO)₃(η^4 -norbornadiene) (frequencies in cm⁻¹; intensities in arbitrary units with same scaling factor as in Table I)

	freq ^a	intens ^b	freq ^c	intens ^d	freq ^e		label ^f
					calc	expt	
all ¹² CO	2037.4	0.767	2037.4	0.767	2038.4	2038.6	a
	1969.4	2.231	2027.1	1.703	2028.1	2028.4	1
			2014.0	1.256	2015.0	2014.8	2
mono ¹³ CO	2027.1	1.703	1990.5	0.278	1991.5	1991.0	p
	1969.4	2.424	1969.4	4.655	1971.4	1971.7	3
	1933.8	2.288	1946.4	1.642	1948.4	1949.2	4
			1933.8	2.288	1935.8	1930 ^g	5
			1924.1	2.484	1926.1		6
bis ¹³ CO	2014.0	1.256	1924.1	2.484	1926.1		
	1946.4	1.642					
	1924.1	1.675					
all ¹³ CO	1990.5	0.278					
	1924.1	0.809					

^a Calculated using $k = [(2k_{\text{eq}} + k_{\text{ax}})/3] = 1603.52$ and $k' = [(2k_{\text{ax,eq}} + k_{\text{eq,eq}})/3] = 36.68 \text{ Nm}^{-1}$; reduced mass ratio = 0.97698. ^b The "I" matrix, which contains bond angle data, was kept the same as in Table I; in fact, changing this matrix made little difference to the intensities. ^c Grouping of bands in numerical order. ^d Intensities appropriately summed. ^e To allow for solvent effects 1 cm^{-1} and 2 cm^{-1} have been added to the upper four and lower four bands, respectively. ^f Bands a and p are the unaffected in-phase all¹²CO and all¹³CO bands. ^g Very broad band which appears to consist of two broad unresolved bands.

eraging the wavenumbers (or frequencies) and averaging the force constants of the two CO groups. Where a metal complex contains several different CO groups, vibrationally coupled together, the situation becomes more complex. However, the $\nu(\text{CO})$ frequencies are well separated from the frequencies of other normal modes; hence the F matrix contains only principal and interaction CO force constants. Although in such cases the boundary condition of keeping the sum of wavenumbers constant is not strictly obeyed, it seems justified to average the energy factored CO force constants to predict the $\nu(\text{CO})$ pattern in the fast exchange limit. Clearly predicting a spectrum in any intermediate situation will be far more difficult, the more so since the validity of a treatment analogous to the NMR Bloch equations is still under discussion.^{2-4,20}

In the static structure of **1** there are two CO groups with force constant k_{eq} , and one CO group with k_{ax} . Thus, for an averaged force constant it is appropriate to take $k = (2k_{\text{eq}} + k_{\text{ax}})/3$. Similarly, the averaged interaction constant will be taken as $k' = (2k_{\text{ax,eq}} + k_{\text{eq,eq}})/3$. Retaining the same reduced mass ratio as for the "frozen" molecule, the frequency data listed in Table II have been calculated for each of the isotopomers in the fast exchange limit. Comparing these data with those in Table I, we note that the possible violation of the boundary condition (constancy of the sum of the frequencies) is not significant. It is now clear what band pattern is to be expected. As anticipated the three-band spectra of both the all¹²CO and all¹³CO species will collapse into two-band patterns associated with the (pseudo)-C_{3v} symmetry, but it is important to note that the high-frequency in-phase vibrations are only marginally shifted so that *in practice* these bands will appear to be unaffected by the exchange process. In addition, the two low-frequency out-of-phase bands for each species should collapse to a single band at almost the mean position; this, of course, is what has been previously observed⁵ for the all¹²CO species and is shown in Figure 2. As stated in section a, the six bands associated with the monoax¹³CO and monoeq¹³CO species should collapse to a set of three bands and similarly for the bis¹³CO species. In particular, the positions of each of the high-frequency in-phase vibrations are expected to be at the statistically weighted means of the "frozen" molecules.

In order to make a detailed comparison of the calculated spectrum with the experimental one, we need to make some allowance for solvent shifts. The in-phase high-frequency bands of the all¹²CO and all¹³CO molecules (a and p in Figure 5) in scXe

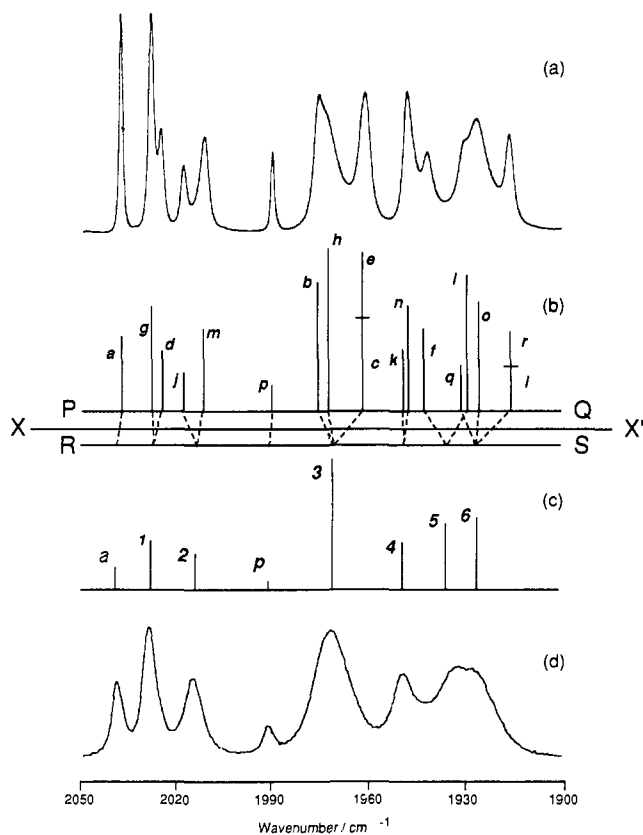


Figure 9. (c) Calculated averaged $\nu(\text{CO})$ spectrum for the ¹³CO-enriched (42%) **1** as described in the text and in Table II, correlated with (d) the experimental spectrum at ambient temperature (Figure 7c), and (a and b) the experimental and calculated low-temperature spectra (Figures 5b and 5c).

at 25 °C (Figure 7c) are shifted up in frequency by about 1 cm^{-1} from the frequencies in Figure 7a. Following these and other observations,¹⁹ we add 1 cm^{-1} to the calculated values of the high-frequency in-phase vibration bands and 2 cm^{-1} to the rest. These numbers are listed in Table II, and the spectrum is plotted in Figure 9. Figure 9d shows again for comparison the spectrum of **1** in scXe at 25 °C.

The agreement between the calculated and experimental spectra is clearly very good. To make a direct comparison with the low-temperature spectrum, Figures 9a and 9b repeat Figures 5b and 5c. Certain points are worth noting. Bands a and p have broadened in scXe at ambient temperature only by an amount to be expected on the basis of general solvent effects (as the high-frequency band in Figure 2). Bands d/g and j/m have collapsed to single bands (labeled 1 and 2) which are broader than a and p; this implies (again as in Figure 2, but now for the low-frequency features) that collapse has not proceeded quite to completion. To visualize what may be happening upon raising the temperature, the calculated "frozen" (Figure 9b) and "rapid exchange" (Figure 9c) spectra are connected as shown. The lines PQ and RS represent, respectively, the "frozen" and "rapid exchange" extremes. If the spectrum at an intermediate stage of collapse follows the dotted lines, then line XX' may represent an intermediate spectrum. This provides a neat explanation of the variation in bandwidths; for instance, band 4 derives from two "frozen" bands which are very close together and hence on collapse they should display a narrow band, as is observed. By contrast, bands 5 and 6 derive from one and two pairs of bands, respectively, quite widely separated in the "frozen" spectrum and hence produce a rather square-looking shape due to the overlap of the resulting two bands in the rapid exchange limit. Similar arguments apply to the other bands. The spectral changes on increasing the temperature in scXe from 25 °C to 88 °C are modest (see Figures

(20) MacPhail, R. A.; Strauss, H. L. *J. Chem. Phys.* **1985**, *82*, 1156. Wood, K. A.; Strauss, H. L. *Ber. Bunsenges. Phys. Chem.*, **1989**, *93*, 615.

7c and 7d) but are consistent with the line XX' moving closer to the line RS. In particular, over and above general solvent broadening, bands 1, 2 and 3 become slightly narrower: this is consistent with the observations on the unlabeled complex **1** shown in Figure 2.

Conclusions

As far as we are aware, this is the first example of a compound that illustrates clear IR coalescence which can be predicted on the basis of a very simple model. The complicated $\nu(\text{CO})$ spectrum of 42% ^{13}C -enriched $\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ in LKr/Xe at low temperatures can be accurately fitted with the four parameters considered in the energy-factored CO force field appropriate for the $\text{M}(\text{CO})_3$ group under C_s symmetry. Warming the molecule to high temperature in scXe produces dramatic spectral changes including band broadening and coalescence. The appearance of the high-temperature "rapid exchange" spectrum can be predicted using the two parameters appropriate for the $\text{M}(\text{CO})_3$ group under (pseudo)- C_{3v} symmetry, which are obtained by statistically averaging the above four parameters.

We are aware that this is not the complete story, but only the first step toward the final goal of extracting kinetic data from variable-temperature IR spectra, which would then allow the evaluation of activation parameters for the exchange process. On the other hand, it would be very appealing to establish dynamic IR spectroscopy as a tool for gaining insight into very fast processes, associated with extremely low barriers, far below the 5–6-kcal mol⁻¹ accessible by dynamic NMR spectroscopy. But, on the other hand, such a low barrier makes the potential wells very flat, and in consequence of this there can be some contribution to the spectra from molecules in higher levels within the potential wells and above the exchange barrier. Details of these considerations and calculations will be published elsewhere.

Experimental Section

$\text{Fe}(\text{CO})_3(\eta^4\text{-norbornadiene})$ (**1**) and $\text{Fe}(\text{CO})_3(\eta^4\text{-butadiene})$ (**2**) were synthesized according to established procedures.²¹ Isotopically labeled carbon monoxide (99% ^{13}C , <1% ^{18}O ; CLM-1845, Cambridge Isotope Laboratories, Woburn/MA, USA) was purchased from Promochem (Wesel/Germany). The ^{13}C enrichment of **1** was performed by irradiation of 0.2 g of the complex in *n*-pentane (50 mL) under ^{13}C atmosphere (70 mL, ca. 1.2 bars) until the high-frequency band of the starting material was reduced in intensity by a factor of ca. 5. After evaporation under vacuum, the residual solution (ca. 3 mL) was cooled to dry ice temperature, whereupon yellow crystals precipitated and were separated from the supernatant solution and dried under vacuum. Mass spectral analysis showed the following composition of the $\text{Fe}(\text{CO})_3\text{-}n(^{13}\text{C})_n$ ($\eta^4\text{-norbornadiene}$) sample: 19% ($n = 0$), 43% ($n = 1$), 31% ($n = 2$), and 7% ($n = 3$). Krypton and xenon (BOC Research Grade) were used without further purification. The cells for IR spectroscopy in liquid noble gas solvents at low temperature and in supercritical fluids have been described elsewhere.^{9,10} Spectra in these solvents were run on either Nicolet 7199 (with MX-3600 data station) or Nicolet 730 FTIR instruments. The spectra in hydrocarbon solvents were run on a Perkin-Elmer 1760 FTIR instrument (with PE 7500 data station) using a low-temperature cell (1-mm pathlength, CaF_2 windows, cooled with nitrogen gas), which will be described elsewhere.²²

Acknowledgment. We thank the Science and Engineering Research Council and the EEC (SCIENCE Contract ST007) for support. We acknowledge helpful discussions with Professors H. L. Strauss, I. M. Mills, and M. Poliakoff and with Dr. S. A. Jackson, and skillful technical assistance from Mr. J. M. Whalley, Mr. D. R. Dye, Mr. K. Schneider, and Mr. K. Kerpen.

(21) For a review see: King, R. B. In *The Organic Chemistry of Iron*: Koerner von Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New York, 1987, Vol. 1, p 525.

(22) Klotzbücher, W. E. Manuscript in preparation.

Dye-Sensitized Photooxidation of Vitamin E Revisited. New 7-Oxaspiro[4.5]dec-1-ene-3,6-dione Products by Oxygenation and Ring Contraction of α -Tocopherol

Marco d'Ischia, Claudio Costantini, and Giuseppe Prota*

Contribution from the Department of Organic and Biological Chemistry, University of Naples, Via Mezzocannone 16, I-80134, Naples, Italy. Received February 18, 1991.
Revised Manuscript Received June 11, 1991

Abstract: The dye-sensitized photooxidation of α -tocopherol, the major component of the biological antioxidant vitamin E, was reinvestigated under biomimetic conditions. When methylene blue was used as the sensitizer and ethanol-phosphate buffer (pH 6.8; 7:3, v/v) as the solvent, the reaction led to the formation, besides α -tocopherol quinone (**3**) and its epoxide (**4**), of three hitherto unknown photooxygenation products accounting overall for about 15% of the consumed substrate. These were identified as two diastereoisomers corresponding to the gross structure of 1,2,8-trimethyl-4-methylene-8-phytyl-7-oxaspiro[4.5]dec-1-ene-3,6-dione (**8**) and one diastereomer of the hydrated derivative 4-hydroxy-1,2,4,8-tetramethyl-8-phytyl-7-oxaspiro[4.5]dec-1-ene-3,6-dione (**9**). Formation of the 7-oxaspiro[4.5]dec-1-ene-3,6-dione system was envisaged as resulting from a ring-contracting rearrangement of an epoxyquinone hemiketal intermediate (**10**) or a related species arising from singlet oxygenation of α -tocopherol.

Introduction

Vitamin E, which occurs mainly in the form of α -tocopherol, occupies a central position in the defense armamentarium of living cells against lipid peroxidation and membrane damage accompanying oxidative stress conditions.^{1,2} The biological activity of α -tocopherol stems primarily from the ability to act as an efficient

chain-breaking antioxidant, trapping reactive peroxy radicals and competing with oxidizable unsaturated lipids during aerial oxidation processes.^{3,4}

There is, in addition, more than suggestive evidence that α -tocopherol exerts a fundamental protective function against those

(1) Machlin, L. J. *Vitamin E: A Comprehensive Treatise*; Marcel Dekker: New York, 1980.

(2) Green, J.; McHale, D. In *Biochemistry of Quinones*; Morton, R. A., Ed.; Academic Press: London, 1965; pp 261–285.

(3) Burton, G. W.; Ingold, K. U. *Acc. Chem. Res.* **1986**, *19*, 194–201 and references cited therein.

(4) Kagan, V. E.; Bakalova, R. A.; Zhelev, Zh. Zh.; Rangelova, D. S.; Serbinova, E. A.; Tyurin, V. A.; Denisova, N. K.; Packer, L. *Arch. Biochem. Biophys.* **1990**, *280*, 147–152.