Table I. Vibrational Frequencies for Dioxygen-Bound Complexes[a]

	ν(Fe-O), cm^{-1}	ref
cytochrome oxidase	589	this work
Hb	567	11
Mb	570	9
HRP III	562	9
Im (heme *a*)$Fe^{2+}-O_2$	576	7
(TMP)Fe-O-O-Fe(TMP)	574	6
(Pip)(TPP)$Fe^{2+}-O_2$	575	12
(TPP)$Fe^{2+}-O_2$	509	12

[a] Abbreviations: Hb, hemoglobin; Mb, myoglobin; HRP, horseradish peroxidase; Im, imidazole; Pip, piperazine; TPP, *meso*-tetraphenylporphyrin.

absorption spectrum of the enzyme–CO complex (inset Figure 1) shows a Soret maximum at 430 nm as expected.[4]

Time-resolved resonance Raman spectra of cytochrome oxidase at 10 μs subsequent to carbon monoxide photolysis in the presence of O_2 are shown in Figure 1A–D. Spectrum E is that of the photodissociation product of the reduced carbonmonoxy enzyme (pump-probe delay = 10 ns). Spectrum A, obtained with a low-energy, defocused beam (0.3 mJ), is similar to the 10-ns spectrum with the exception that a new mode appears at 589 cm^{-1}. Figure 1B shows that the 589-cm^{-1} mode in the $^{16}O_2$ spectrum is downshifted to 565 cm^{-1} when the experiment is repeated with $^{18}O_2$. This allows us to assign it as the iron–oxygen stretching motion in the cytochrome a_3^{2+}–O_2 complex, as the 24-cm^{-1} shift is in agreement with that expected from the two-body harmonic oscillator approximation for Fe^{2+}–O_2. Spectra C and D were obtained with relatively high energies (1 mJ), and the absence of modes located at 589 cm^{-1} (Figure 1C, $^{16}O_2$) and 565 cm^{-1} (Figure 1D, $^{18}O_2$) indicates photodissociation of the oxy ligand, as was observed in the high-frequency experiments[2,5] and further supports our assignment of the 589-cm^{-1} mode in the cytochrome oxidase/O_2 complex.

The most reasonable assignment of the 589-cm^{-1} mode is that it arises from a cytochrome a_3^{2+}–O_2 complex. Such an assignment is consistent with the photolability of this species,[2b] but more important, it is in reasonable agreement with $\nu(Fe^{2+}-O_2)$ frequencies observed in other heme Fe^{2+}–O_2 complexes. Table I summarizes several of these frequencies; the 589-cm^{-1} mode for the oxidase intermediate is similar to, but slightly higher than, $\nu(Fe^{2+}-O_2)$ for several dioxygen-bound heme species. Several further points can be made from Table I. First, the $\nu(Fe^{2+}-O_2)$ in the oxidase intermediate is 13 cm^{-1} higher than that of the imidazole–heme *a* Fe^{2+}–O_2 complex, despite the fact that the model compound reproduces the immediate coordination sphere that is expected to occur around the iron in the protein environment. We regard this increase as mechanistically significant, as discussed below. Second, the oxidase species has a frequency that is close to the 574 cm^{-1} observed for the iron–oxygen stretching frequency for the five-coordinate μ-peroxo dimer reported by Nakamoto and co-workers.[6] Despite the similarity in those two frequencies, we nevertheless favor a cyt a_3^{2+}–O_2 structure for the intermediate we detect. The basis for this lies in our expectation that cytochrome a_3 will retain its proximal histidine ligand during catalysis and that this trans ligand will significantly perturb the iron–oxygen stretching frequency in a peroxy a_3 species relative to the five-coordinate model compound.[7] A similar frequency perturbation in the iron–oxygen stretching frequency as a result of trans-ligand effects is apparent in Table I when one compares the five-coordinate (TPP)Fe^{2+}–O_2 complex (ν(Fe–O) = 509 cm^{-1}) to the six-coordinate (Pip)(TPP)Fe^{2+}–O_2 species (ν(Fe–O) = 575 cm^{-1}) and is also apparent in heme ferryl oxo species.[7]

As noted above, the iron–oxygen stretching frequency in the oxidase intermediate is elevated relative to the other systems for which data exist. In fact, it is the highest $\nu(Fe^{2+}-O_2)$ reported for heme iron–dioxygen complexes. This suggests that a stronger Fe–O bond exists in the oxidase intermediate than is normally encountered. Because an inverse relationship between Fe–O and O=O bond strengths is expected, as we argue elsewhere,[7] a weaker O=O bond is thus likely in the cytochrome a_3–dioxygen adduct. Such an observation is consistent with the dioxygen bond cleaving and reducing functions of the oxidase. It also suggests the subsequent formation of a bona fide peroxy intermediate prior to O=O bond cleavage, as has been long suspected in the oxidase catalytic cycle.[2a,8,13]

Acknowledgment. We thank Dr. A. Oertling for stimulating discussions and Deak Watters for machining the mixers. This research was supported by the NIH (Grants GM25480 and DK36263).

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(3) The details of the design and construction of the mixer and jet will be published elsewhere: Varotsis, C.; Babcock, G. T., in preparation. The 427-nm, 10-ns pulses were obtained by pumping stilbene with the third harmonic of a Quanta Ray DCR2A Nd:YAG laser.

(4) Vanneste, W. H. *Biochemistry* **1966**, *5*, 838.

(5) Varotsis, C.; Babcock, G. T., unpublished results.

(6) Paeng, I. R.; Shiwaku, H.; Nakamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 1995.

(7) Oertling, W. A.; Kean, R. T.; Wever, R.; Babcock, G. T. *J. Am. Chem. Soc.*, submitted.

(8) Blair, D. F.; Witt, S. N.; Chan, S. I. *J. Am. Chem. Soc.* **1985**, *107*, 7389.

(9) Van Wart, H.; Zimmer, J. *J. Biol. Chem.* **1985**, *250*, 8372.

(10) Wikström, M.; Krab, K.; Saraste, M. *Cytochrome Oxidase, A Synthesis*; Academic Press: New York, 1981.

(11) Brunner, H. *Naturwissenschaften* **1974**, *61*, 129.

(12) Nakamoto, K.; Paeng, I. R.; Kuroi, T.; Iosbe, T.; Oshio, H. *J. Mol. Struct.* **1988**, *189*, 293.

(13) Wikström, M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4051.

(14) A loose point focus at the sample was used to decrease the probe power density. We estimate that the probe power density used to record spectra A and B was 12-fold less than in spectra C–E.

The Geometry of Reactive Intermediates by Nutation NMR Spectroscopy: The *tert*-Butyl Cation

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The use of superacidic liquid or solid matrices at low temperature permits the study of very reactive carbocations for extended periods of time,[1] and variable temperature NMR studies under these conditions have provided a wealth of dynamic and qualitative structural information.[1,2] By contrast, determinations of the geometry (bond lengths and angles) of carbocation salts by diffraction methods are rare. This is not from lack of effort.[3,4d] Reports of the few successful X-ray studies of reactive carbocations provide ample evidence of the difficulty in obtaining suitable single crystals.[4] To our knowledge, X-ray structures of only two carbocations that are not stabilized by heteroatoms or π-system delocalization have been reported, and both of these have numerous

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(1) Recent reviews include the following: (a) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley: 1985. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: 1985. (c) Ahlberg, P.; Jonsall, G.; Engdahl, C. *Adv. Phys. Org. Chem.* **1983**, *19*, 223.

(2) Saunders, M.; Chandrasekhar, J.; Schleyer, P. v. R. *Rearrangements in Ground and Excited States*; Academic Press: 1980; pp 1–53.

(3) Dinnocenzo, J. P. Ph.D. Thesis, Cornell University, 1985.

(4) (a) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1986**, *108*, 3613–3617. (b) Montgomery, L. K.; Grendze, M. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749–4750. (c) Laube, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 349. (d) Laube, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 560. (e) For a review of earlier work on more stable ions, see: Sundaralingam, M.; Chwang, A. K. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. 5, Chapter 39.

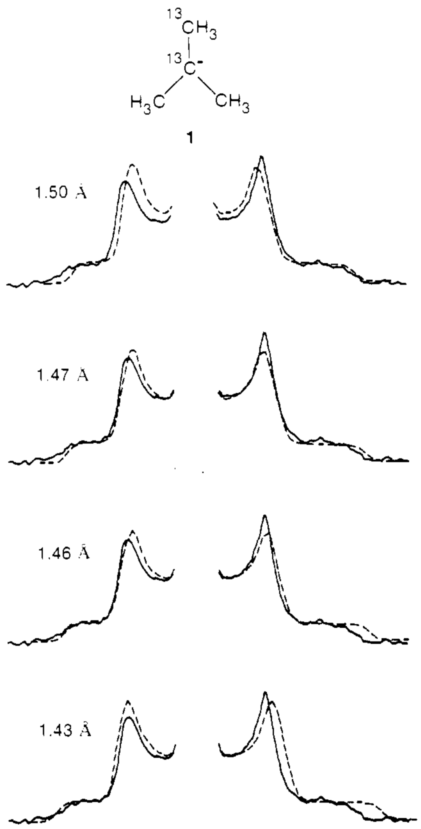

Figure 1. Experimental (solid) and simulated (dashed) nutation NMR spectra of the *tert*-butyl cation doubly labeled with ^{13}C in the central and methyl carbon positions (**1**). The best fit for the ^{13}C–^{13}C distance is between 1.46 and 1.47 Å.

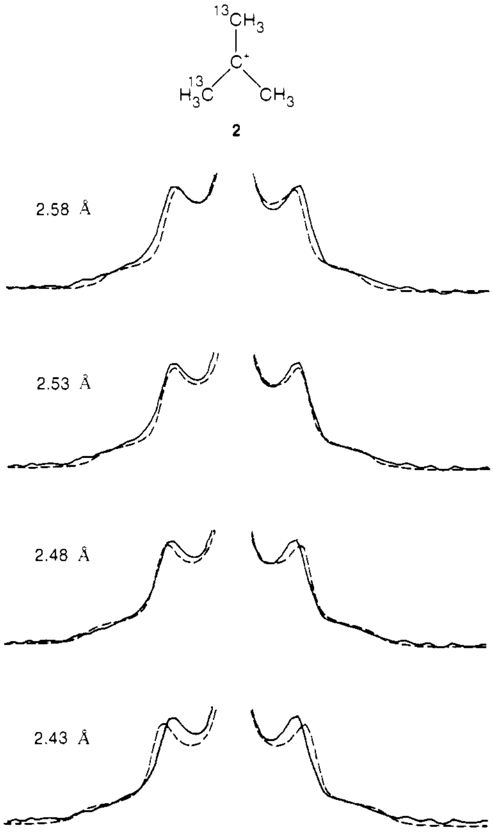

Figure 2. Experimental (solid) and simulated (dashed) nutation NMR spectra of the *tert*-butyl cation doubly labeled with ^{13}C in two of the methyl positions (**2**). The best fit for ^{13}C–^{13}C distance is 2.51 Å.

methyl substituents to minimize lattice disorder problems.[4c,d]

Since nutation NMR spectroscopy is capable of measuring internuclear distances to ~1% accuracy in solids lacking long-range order,[5] this method can be used to obtain localized geometry of reactive carbocations. We report here the geometry of the *tert*-butyl cation, the archetypical carbocation. The nutation method measures the distance between two magnetic nuclei. Therefore, the framework geometry of the *tert*-butyl cation can be determined from experiments on the two doubly ^{13}C-labeled isomers with the ^{13}C-labels on the methyl and central carbons (**1**, Figure 1) and on two of the methyl carbons (**2**, Figure 2).

Polycrystalline samples of **1** and **2** in SbF_5 were prepared from the appropriately labeled *tert*-butyl chloride precursors and loaded by modification of a previously described method.[6] In order to minimize intermolecular ^{13}C–^{13}C dipolar interactions,[5] 6–8% doubly labeled *tert*-butyl chloride diluted with unenriched alkyl chloride was used as a precursor in these preparations. All spectra were obtained at 77 K,[7] to minimize motional averaging and concomitant reduction of the ^{13}C–^{13}C dipolar splitting.[8] Spectra obtained at 170 K do show a significant reduction in spectral width due to such motion. However, spectra obtained at temperatures as low as 12 K give the same splitting as the 77 K spectra, confirming that the measurements at 77 K reflect the rigid-lattice limit and a correspondingly reliable internuclear distance.

Internuclear distances are determined in nutation spectroscopy by comparison of experimental and calculated Pake doublets.[5] The experimental doublet will appear distorted unless the nutation frequency (strength of the rf field expressed in frequency units) is large compared with the ^{13}C chemical shift dispersion. Since the shift dispersion of the cationic carbon in **1** is very large (450 ppm = 6.8 kHz at 1.4 T)[9] and the nutation frequency is 19.2 kHz, an asymmetry is observed. The simulations used to measure the central carbon–methyl carbon distance in **1** include the effects of the chemical shift tensor, since both the magnitude and orientation (determined by symmetry) are known.[9] Comparison of experimental spectra with simulations using a range of intercarbon distances is shown in Figure 1. The best fit for the central carbon–methyl carbon distance is between 1.46 and 1.47 Å. The center line, due to isolated ^{13}C spins, is cropped for clarity but has a negligible effect on the fit of the Pake doublet for the distance measurement.[10] The simulated spectra exhibit an asymmetry owing to the large chemical shift effects as discussed above, but it is noteworthy that the best fit is the same even when the rf field is assumed to be infinitely large compared with the shift dispersion, i.e., when chemical shift effects are completely negligible.

The results of a fit of the distance between the methyl carbons in **2** is shown in Figure 2; the best fit is 2.51 Å. Simulations for **2** were made with the assumption that the chemical shift tensor dispersion of the methyl carbons (40 ppm = 0.6 kHz) is negligible compared with the 5.7 kHz nutation frequency.

The central carbon–methyl carbon bond is almost 0.1 Å shorter than the usual single bond value of ~1.55 Å and is 0.05 Å less than the 1.513 Å calculated for the *tert*-butyl cation at the STO-3G level[11] but is in close agreement with the bond length (1.459 Å) found in a more recent calculation carried out at a much

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(5) (a) Yannoni, C. S.; Kendrick, R. D. *J. Chem. Phys.* **1981**, *74*, 747. (b) Horne, D.; Kendrick, R. D.; Yannoni, C. S. *J. Magn. Reson.* **1983**, *52*, 299.

(6) See: Myhre, P. C.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 230. Samples were prepared by low-temperature high-vacuum (77 K, $<10^{-5}$ Torr) codeposition of the *tert*-butyl chloride with 2 equiv of SbF_5 and excess SO_2ClF, warming to 195 K, stirring, and subsequent vacuum evaporation of SO_2ClF after precipitation. The resulting solid, presumed to be $C_4H_9^+Sb_2F_{10}X^-$ (X = F, Cl), was transferred at low temperature under nitrogen to glass tubes and sealed under vacuum for NMR studies.

(7) Carbon-13 magnetization was generated prior to application of the nutation pulse sequence by cross polarization with the protons.[5] Fluorine as well as proton decoupling was applied during the nutation sequence to minimize heteronuclear broadening.

(8) Gutowsky, H. S.; Pake, G. E. *J. Chem. Phys.* **1950**, *18*, 97.

(9) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201.

(10) Yannoni, N.; Kahr, B.; Mislow, K. *J. Am. Chem. Soc.* **1988**, *110*, 6670.

(11) Hehre, W. J. *Acc. Chem. Res.* **1975**, *8*, 369.

higher level (MP2/6-31G*).[12] The C–C–C bond angle calculated by using 1.46 and 2.51 Å for the central-methyl and methyl–methyl distances is 120° within experimental error, providing a clear experimental verification of the traditional bonding model. Thus, nutation NMR shows that the structure of the *tert*-butyl cation is trigonal with a short (1.46 Å) central carbon–methyl carbon bond length.

We have demonstrated a general methodology for measuring the molecular geometry (bond lengths and angles) of carbocations by using nutation NMR spectroscopy. It should be possible, by using nutation NMR, to obtain the localized geometry of many reactive intermediates that can be stabilized in a matrix. Preparation of doubly-^{13}C labeled isomers of several other interesting carbocations is in progress.

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Registry No. *tert*-Butyl cation, 14804-25-2; *tert*-butyl chloride, 507-20-0.

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[12] Seeger, U.; Liu, B.; DeFrees, D. J., private communication.

The Carbon-13 NMR Spectrum of Solid Iron Pentacarbonyl

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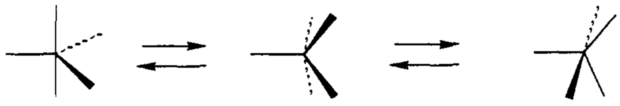
For the first time the carbon-13 NMR signals for the axial and equatorial carbonyls in iron pentacarbonyl have been observed. The detection of these signals in the solid suggests that axial–equatorial exchange in the solid state cannot occur at a rate greater than 10^2 s^{-1} at −38 °C or lower.

The first carbon-13 NMR spectrum of a metal carbonyl was reported in 1958 for iron pentacarbonyl by Cotton, Danti, Waugh, and Fessenden.[1] The result, a single resonance in the carbonyl region, has been shown to be correct by several subsequent investigations;[2-4] in fact the single resonance for $Fe(CO)_5$ persists to −160 °C.[4] Since the structure of iron pentacarbonyl in solution is trigonal-bipyramidal, the carbon-13 NMR spectrum for this complex should contain two signals of relative intensity 2 to 3. Of the possible explanations for the single resonance it is now accepted that the trigonal-bipyramidal structure undergoes a reorientation which is fast on the NMR time scale and exchanges equatorial and axial carbonyl resonances. The most likely mechanism for the exchange of carbonyls is the well-known Berry pseudorotation[5] shown schematically below.

Berry Rotation



Iron pentacarbonyl has been previously studied in the solid state by broadline NMR at temperatures from 4.2 to 213 K.[6] Evaluation of the spin lattice relaxation times over part of this temperature range and calculation of the expected line shapes led to the conclusion that a molecular rearrangement occurs in solid $Fe(CO)_5$. Two possible mechanisms for the motion were considered, a pseudorotation, as described above, and a rotation about the molecular 3-fold axis of the trigonal-bipyramidal molecule. The authors concluded that a Berry pseudorotation better described the experimental data.[6] The exchange frequency for the motion was measured to be 2.4 × 10^4 s^{-1} at −60 °C. From the reported variation of the rate with temperature an activation energy of 0.5 kcal mol^{-1} can be calculated. Although the activation energy is similar to what is estimated for axial–equatorial exchange of carbonyls in liquid $Fe(CO)_5$, the exchange frequency is much slower than the corresponding rate of molecular reorientation in liquid $Fe(CO)_5$ at −20 °C (1.1 × 10^{10} s^{-1}).[7,8] The rate estimated from the broadline studies in the solid state is sufficiently fast to exchange axial and equatorial carbonyl resonances on the NMR time scale provided the isotropic chemical shifts of the axial and equatorial carbonyl groups are within 1000 Hz. The expected chemical shift difference at 22.5 MHz for axial and equatorial carbonyls should be less than this since the typical range of chemical shifts observed for terminal carbonyl ligands in neutral iron carbonyl derivatives is ca. 208–220 ppm.[9]

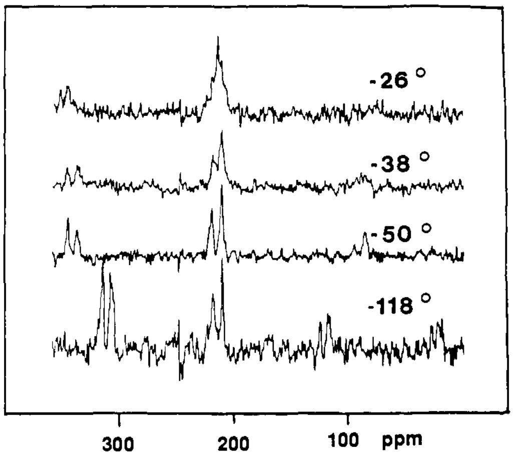


Figure 1. Magic angle spinning ^{13}C NMR spectra of solid $Fe(CO)_5$. The spinning rate varied from 2140 Hz at −118 to 2900 Hz at −26 °C.

Figure 1 shows the magic angle spinning ^{13}C NMR spectra for iron pentacarbonyl as a function of temperature.[10] At temperatures of −38 °C and lower, two signals at 216.0 and 208.1 ppm are observed. The relative integrated intensities, including spinning sidebands, are 2:3, respectively, for the two signals consistent with a trigonal-bipyramidal structure. This represents the first time that distinct axial and equatorial signals have been observed in a metal pentacarbonyl complex.

The melting point of $Fe(CO)_5$ is approximately −20 °C. All MAS spectra recorded between the temperatures −20 and −30 °C show three signals in the carbonyl region. These occur at 216.0, 208.1, and 211.6 ppm. The last of these corresponds to the isotropic shift of iron pentacarbonyl.[3] The presence of this signal however is not indicative of rapid axial–equatorial exchange in

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[1] Cotton, F. A.; Danti, A.; Waugh, J. S.; Fessenden, R. W. *J. Chem. Phys.* **1958**, *29*, 1427.

[2] Bramley, R.; Figgis, B. N.; Nyholm, R. S. *Trans. Faraday Soc.* **1962**, *58*, 1893.

[3] Mann, B. E. *J. Chem. Soc., Chem. Commun.* **1971**, 1173.

[4] Jesson, J. P.; Meakin, P. *J. Am. Chem. Soc.* **1973**, *95*, 1344.

[5] Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

[6] Spiess, H. W.; Grosescu, R.; Haeberlen, U. *Chem. Phys.* **1974**, *6*, 226.

[7] Spiess, H. W.; Mahnke, H.; *Ber. Bunsen Gesell.* **1972**, *76*, 990.

[8] Sheline, R. K.; Mahnke, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 314.

[9] Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1974**, *77*, 1.

[10] The MAS spectra were recorded on a spectrometer consisting of a 2.1 superconducting magnet (Chemagnetics), a JEOL FX90Q consol, and a variable-temperature MAS probe tuned to 22.53 MHz (Chemagnetics). Iron pentacarbonyl was enriched to ca. 15% in ^{13}CO by stirring the neat liquid under ^{13}CO in the presence of Palladium black. The sample was distilled and then transferred to a standard delrin rotor at −78 °C. The probe was precooled prior to −30 °C before the sample was introduced. All spectra obtained are the result of a single 90° pulse (6 μs) at the temperature indicated. Prior to obtaining a spectrum the temperature, as indicated by a thermocouple in the drive gas stream, was held constant for 10 min. After recording a spectrum and before recording the next spectrum the sample was warmed to between −23 and −30 °C for 0.5 h to allow the carbon magnetization to relax. The sample was then recooled to the desired temperature.