catalytically active species, which is supported by high-pressure infrared measurements. A dependence on H_2 partial pressure between first and second order (ca. 1.3) is observed, suggesting an equilibrium involving H_2 prior to the rate-determining step. The formation of methanol in these reactions exhibits the same behavior with respect to H_2 and CO partial pressures, and only minor changes in product distribution are observed on changing the gas composition or pressure.

A mechanistic sequence consistent with all of these observations is shown in Scheme I. Reaction of $Ru(CO)_5$ with H_2 has been observed[20] by high-pressure infrared spectroscopy to produce $H_2Ru(CO)_4$ (step 2). Although an isolated example of hydride migration to coordinated CO has not yet been observed, this appears to be a reasonable first step in CO hydrogenation by this system. Reductive elimination of the resultant formyl ligand could yield coordinated formaldehyde (step 4), as previously proposed in a mechanism for the Fisher–Tropsch reaction.[21] Since this catalytic system is highly specific for methanol formation in the absence of carboxylic acids, a methoxy ligand rather than a hydroxymethyl ligand is presumed to be the methanol precursor; the latter might be expected to yield at least traces of longer chain products. Insertion of formaldehyde into a Ru–H bond to give the methoxy ligand (step 5) could presumably occur in both the presence and the absence of carboxylic acids. However, the formation of a metal–carbon-bonded intermediate (step 6) has been written requiring a carboxylic acid to account for the observed effect of these compounds on glycol formation by this system. This step perhaps involves acylation[22] of a coordinated formaldehyde intermediate by a hydrogen-bonded acid dimer or protonated acid molecule, which would be consistent with the observed high dependence of the glycol formation rate on acid concentration[23] (Figure 1). A related osmium complex containing coordinated formaldehyde has been shown to undergo electrophilic attack by $CF_3SO_3CH_3$ at the oxygen atom, yielding a metal–carbon-bonded methoxymethyl product.[25] The analogous acyloxymethyl product formed by step 6 is presumed to be a glycol precursor, leading to glycol esters through successive CO insertion, reductive elimination, and hydrogenation.[26] Model studies with a related manganese acyloxymethyl complex have demonstrated that these steps can occur even under mild conditions.[27] The presence of a longer chain product, glycerine, can also be accounted for by extension of this scheme with a glycolaldehyde (ester) intermediate. Ethylene glycol has been reported to be a product of cobalt-catalyzed reactions under moderate pressures, and a similar scheme for glycol formation was presented.[3]

Overall rates of carbon monoxide hydrogenation in these catalytic reactions (in several types of solvents) are nearly equal to those recently reported for a similar ruthenium system operated at much higher pressure—for example, a rate of 8.3×10^{-3} turnovers s^{-1} was observed in reaction 4, Table I, as compared with a reported[8] rate (to methanol and methyl formate) of 1.05×10^{-2} s^{-1} at 270 °C under 1300 atm in THF solvent. This comparison exhibits the importance of solvent effects in homogeneous catalysis, even when the catalyst is presumably uncharged and mononuclear; rate improvements obtainable by large increases in pressure may also be achieved by appropriate choice of solvents. An even more important role of reactive, carboxylic acid solvents in this system is demonstrated by the discovery that they cause formation of a two-carbon product by a catalyst which otherwise produces only methanol. The function of this unique solvent/promoter is apparently to intercept a catalytic intermediate and change the course of its reaction. Further research based on these results is in progress.

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[22] Reactions done in solutions of acetic anhydride also produce ethylene glycol diacetate. However, much of the anhydride is hydrogenated under reaction conditions, yielding ethyl acetate and acetic acid.

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[26] Some of the methyl ester produced in carboxylic acid solvents is very probably formed by reductive elimination of an acyloxymethyl ligand; model studies have demonstrated this pathway.[27]

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Resonance Raman Spectra of (Dioxygen)(porphyrinato)(hindered imidazole)iron(II) Complexes: Implications for Hemoglobin Cooperativity

Sir:

We report Fe–O_2 stretching frequencies, determined via resonance Raman (RR) spectroscopy, for oxygenated 1-methyl-, 2-methyl-, and 1,2-dimethylimidazole (1-MeIm, 2-MeIm, and 1,2-diMeIm) adducts of the Fe(II) complex of "picket fence" porphyrin,[1] *meso*-tetrakis[α,α,α,α-[(*o*-pivaloyl)amido]phenyl]-porphyrin, $H_2TpivPP$. The solution ν_{Fe-O_2} frequency of the 1-MeIm adduct has previously been shown[2] to differ by only 1 cm^{-1} from that of oxyhemoglobin[3] (O_2Hb, 567 cm^{-1}). This relatively high frequency suggested appreciable Fe–O_2 multiple bonding,[2] consistent with the short Fe–O_2 bond length, 1.75 Å, obtained from the crystal structure of the 1-MeIm adduct.[4]

A substantially longer Fe–O_2 bond, 1.90 Å, has been determined[5] for the 2-MeIm adduct. The 2-methyl group hinders the approach of the 2-MeIm-bound Fe to the porphyrin plane. This ligand was introduced by Collman and Reed[6] to prepare 5-coordinate high-spin Fe(II) porphyrins, analogues of deoxyhemoglobin. Nevertheless, O_2 does bind to the 2-MeIm adduct, but the Fe atom is somewhat out of the plane,[5] away from the O_2, and the 2-MeIm–Fe bond is also slightly stretched, relative to the 1-MeIm–Fe bond.[4]

The structure of the 2-MeIm adduct was determined with crystals in which one ethanol molecule is hydrogen bonded to each 2-MeIm N-1 proton.[5] We have determined the RR spectrum of this material at low temperature, with low laser power levels, in a spinning sample cell, to minimize possible artifacts due to laser heating. At –70 °C, the Fe–O_2 frequency was located at 561 cm^{-1}. Under the same conditions, a frequency of 572 cm^{-1} was observed for the 1-MeIm adduct. As the temperature was allowed to rise, these bands broadened and shifted to lower frequency (Figure 1). This temperature effect may be due to the population of multiple Fe–O_2 rotational conformations, consistent with the orientational disorder observed in the crystal structures.[4,5] The 1,2-diMeIm adduct, whose structure is not available, gave frequencies similar to those of the 2-MeIm adduct. These results are summarized in Table I.

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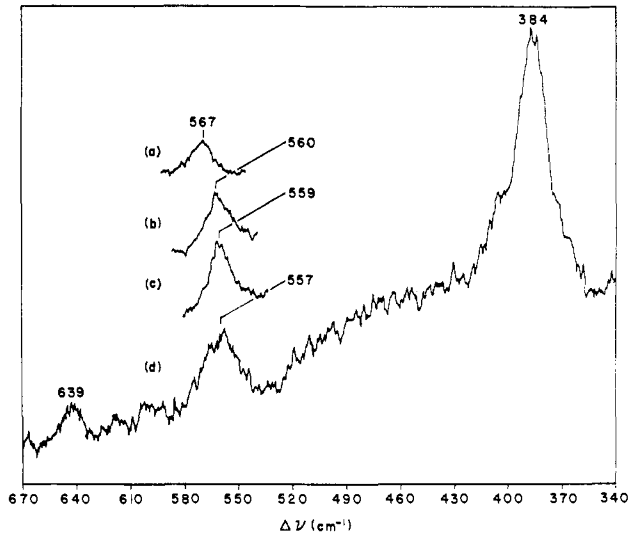

Figure 1. Low-frequency resonance Raman spectra of Fe(TpivPP)LO_2: (a) L = 1-MeIm, (b) L = 1,2-diMeIm, (c and d) L = 2-MeIm·EtOH. Spectra were obtained by using 454.5-nm excitation; 10-cm^{-1} spectral band-pass. (a–c) Sample temperature −20 °C, 50.0-s time constant; (d) sample temperature +25 °C, 5.0-s time constant. Samples were prepared under O_2; for the 2MeIm·EtOH adduct, O_2 was saturated with ethanol vapor. Samples were irradiated in spinning NMR tubes in the back-scattering geometry. Low temperature was obtained by utilizing an optical Dewar through which cold N_2 was passed. This device will be discussed elsewhere.[14] A cylindrical lens was employed to produce a line focus of the laser light to minimize sample damage.

Table I. Frequencies (cm^{-1}) of the Iron–Oxygen Stretching Vibrations[a]

	−70 °C	−40 °C	−20 °C	+25 °C	$P_{1/2}$[b]
Fe(TpivPP)(1-NMeIm)O_2					
solid	572	570	567	567[c]	0.49
CH_2Cl_2 solution		570		568	
Fe(TpivPP)(2-MeIm)O_2·EtOH					
solid	561	560	559	557	620
Fe(TpivPP)(1,2-diMeIm)O_2					
solid	561	560	560	558[d]	43
CH_2Cl_2 solution		567		564	

[a] Frequencies measured to ±1 cm^{-1} by using the 993-cm^{-1} line of Na_2SO_4 (solids) or the 703-cm^{-1} line of CH_2Cl_2 (solutions) as frequeny standards. [b] O_2 pressure of half-saturation (torr) at 25 °C; note that Fe(TpivPP)-(1,2-diMeIm) binds O_2 in a cooperative manner in the solid state and that 43 torr represents the overall pressure ($P_{1/2}$ = 38 torr at 25 °C). [c] $\nu_{Fe-^{18}O_2} = 538$ cm^{-1}; diatomic harmonic oscillator prediction, 541 cm^{-1}. [d] $\nu_{Fe-^{18}O_2} =$ 532 cm^{-1}; diatomic harmonic oscillator prediction, 533 cm^{-1}.

We conclude that the introduction of a methyl group at the 2-position of the imidazole ligand on the FeTpivPP-O_2 adduct lowers ν_{Fe-O_2} by 8–11 cm^{-1}, depending on the temperature. This is an appreciable change, but much less than we had expected from the 0.15-Å bond length difference (combined standard deviation of 0.02 Å) seen in the crystal structures.[4,5] Badger's rule[7] predicts a difference of only ~0.01 Å for a 10-cm^{-1} decrease. This empirical rule, developed for diatomic molecules, may, however, not be reliable for the sterically crowded molecules under consideration here. Warshel[8] has recently performed semiempirical energy calculations on the 2-MeIm adduct, which suggest that the steric effect should be expressed mainly as a tilt of the imidazole away from contact with the porphyrin ring (an effect seen in the crystal structure[5]) with modest stretching of the Fe–2-MeIm and Fe–O_2 bonds. The resulting Fe–O_2 frequency shift is predicted to be 10 cm^{-1}.

In keeping with the crystallographic data, the steric hindrance of the bound imidazole has a dramatic influence on the observed O_2 affinities,[5b,9] as seen in Table I. Though the trend of ν_{Fe-O_2} and $P_{1/2}$ match, the modest range of ν_{Fe-O_2} implies that the difference in ΔG of O_2 binding between Fe(TpivPP)(1-MeIm) and Fe(TpivPP)(2-MeIm)·EtOH (4.2 kcal/mol) cannot be localized in the Fe–O bond.

The resonance Raman spectra of these O_2 complexes show somewhat different behavior in solution than in the solid state (Table I). The effect of the 2-methyl group is less pronounced. The 2-MeIm adduct is oxidatively unstable in solution,[9,10] but we were able to examine the 1,2-diMeIm adduct. The Fe–O_2 frequency is significantly higher in CH_2Cl_2 solution than in the solid samples, and is only 3–4 cm^{-1} below that of the 1-MeIm adduct. The steric influence of the 2-methyl group on ν_{Fe-O_2} seems to be relaxed somewhat in solution.

The O_2 affinity of the 1-MeIm adduct is similar to that of myoglobin, or R-state Hb.[9,10] With 2-MeIm or 1,2-diMeIm as ligands, the affinity is lowered to about that of T-state Hb.[9,10] It was therefore reasonable to suggest[5,9,10] that these adducts were in fact models for T-state HbO_2, in the sense that the steric hindrance provided by the 2-methyl group can serve as an analogue for the protein-induced restraint on the proximal imidazole, which is a central feature of the "tension" model of Hb cooperativity.[12] Recently, Nagai et al.[13] have recorded Fe–O_2 RR bands for Hb Kansas and Hb Milwaukee, mutant Hbs whose ligated forms can be switched to the T quaternary state by the addition of inositol hexaphosphate. They reported that no frequency differences greater than 3 cm^{-1} could be seen between R and T states, whereas a ~10-cm^{-1} decrease might be expected on the basis of the present model results; Warshel[8] has calculated that if the entire 3.6 kcal/heme energy of cooperativity were expressed as proximal imidazole tension the predicted Fe–O_2 frequency decrease would be 20 cm^{-1}. The RR results therefore militate against a significant role for localized tension in ligated T-state Hb, for the mutant Hbs so far examined.

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