Carbon monoxide photolability in copper(I) carbonyl complexes and fast CO/O_2 (re)binding

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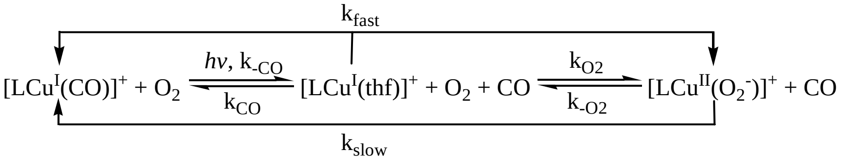
In heme proteins and their synthetic models, carbon monoxide acts as a competitive inhibitor of dioxygen and is often used as a redox-inactive surrogate for gaining further insight into primary metal-ligand interactions. Recently we have applied this to copper containing complexes as models for copper proteins. Kinetic and thermodynamic parameters for the reactions of O_2 and CO with $[Cu^I(TMPA)]B(C_6F_5)_4$ {tmpa = tris(2-pyridyl)methyl]amine} were determined using a “flash-and-trap” method. This technique involves single wavelength excitation (λ_{ex} = 355 nm) into the MLCT band of $[Cu^I(L)(CO)]^+$ resulting in CO photodissociation, which in turn reveals a labile or empty coordination site whereupon O_2 binds, producing a cupric-superoxo species; at this point, CO subsequently displaces dioxygen, reforming the ground state complex. The rate of CO binding in THF solvent at 298 K ($k_{CO} = 1.92 \times 10^9\ M^{-1}s^{-1}$) was obtained in the absence of O_2. [*Inorg. Chem.* **2001**, *40*, 4514.] In tetrahydrofuran when mixtures of O_2 and CO are introduced at low temperatures (188–218 K), both “fast” and “slow” processes provide data for the forward reaction, k_{O2} ($\Delta H^\ddagger$ = 7.62 kJ mol^{-1}, $\Delta S^\ddagger$ = –45.1 J mol^{-1} K^{-1}). The “slow” process provides information for the reverse reaction, k_{-O2} ($\Delta H^\ddagger$ = 58.0 kJ mol^{-1}, $\Delta S^\ddagger$ = 105 J mol^{-1} K^{-1}) and the overall thermodynamic parameters (ΔH° = –48.5 kJ mol^{-1}, ΔS°= –140 J mol^{-1} K^{-1}). The temperature dependent data can be extrapolated to room temperature (298 K) to give the following data: $k_{O2} = 1.3 \times 10^9\ M^{-1}\ s^{-1}$, $k_{-O2} = 1.5\times10^8\ M^{-1}\ s^{-1}$, and K_{O2} = 15.4 M^{-1}. The rate of O_2–binding exceeds that for hemes. [*J. Am. Chem. Soc.* **2003**, *125*, 11866.]



We will also discuss research involving extension of the “flash-and-trap” method to other copper systems. Both tetradentate, R-TMPA {R=H, MeO, NMe_2}, and tridentate systems, R-PY1 {PY1= bis(2-picolyl)amine; R= PhOH, PhOMe, Me, Bn} are being examined to see how changes in the ligand affect the photophysical properties and/or the CO/O_2 binding kinetics.