



Homogeneous Oxidative Coupling Catalysts: Kinetics of the Oxidation of Copper(I) Complexes [(Pyr)_nCuX]₄ (n = 1 or 2, Pyr = pyrrolidine, X = Cl, Br or I) by Dioxygen in Aprotic Media

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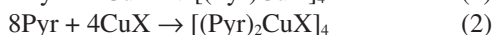
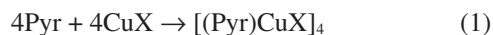
This paper reports the kinetics of oxidation of [(Pyr)_nCuX]₄ by O₂ to form the oxidative coupling catalysts [(Pyr)_nCuX]₄O₂. The mechanism has been described as a pre-equilibrium, K, between tetranuclear copper(I) and incoming dioxygen, which is followed by rate determining step k₂. The rates of the reaction are reflected to the core structure of [(Pyr)_nCuX]₄, faster for cubane structure as for (X = Cl or Br), when compared to step structure as in case of (X = I). The overall reaction is a second-order process, first order in each [(Pyr)_nCuX]₄ and [O₂], with rate constant k_{on} (k_{on} = Kk₂) and exothermic ΔH° varying from -4.9 to -15.5 kcal mol⁻¹ and ΔS° varying from -61.3 to -97.8 cal deg⁻¹ mol⁻¹. k_{on} were found to be very sensitive to n value 1 or 2.

Key Words: Mechanism, Tetranuclear oxocopper(II) formation, Homogeneous oxidation, Coupling catalysts.

INTRODUCTION

The study of homogeneous oxidative coupling cycle of phenols by copper catalysts is very important, from the catalytic industry point of view, as well as understanding model for tyrosinase copper protein¹⁻⁶.

Copper(I) halides react quantitatively with pyrrolidine (Pyr) in dioxygen-free methylene chloride or nitrobenzene to form tetranuclear copper(I) complexes [(Pyr)_nCuX]₄; n = 1 or 2, X = Cl, Br or I.



These complexes are soluble and completely reduce dioxygen to dioxo bridging ligand, with stoichiometry, Δ[Cu(I)]/Δ[O₂] = 4.0. Analytical and cryoscopic data establish the formation of discrete tetranuclear products. The stable oxo solids [(Pyr)_nCuX]₄O₂ mimic tyrosinase copper protein. They act as a homogeneous oxidative coupling catalyst for phenols⁷.



Electronic transition spectra, (Fig. 1), in the near infrared for [(Pyr)_nCuX]₄O₂ are explained as charge transfer from a minimum of three halo ligands to a copper(II) site, (LMCT). Therefore one can expect a higher molecular absorptivity when X = I, as exactly in [(Pip)_nCuX]₄O₂ system⁴. However, it is about half of what is expected. The lower absorptivity explains

the step structure of [(Pyr)_nCuI]₄O₂, **Scheme-I**, in which only two copper(II) sites, instead of four as in [(Pyr)_nCuX]₄O₂, X = Cl or Br, have three iodo ligands per copper center. In addition to infrared and electronic spectra for [(Pyr)_nCuI]₄O₂, more EPR bands are observed and it is concluded that two different types of copper(II) sites are present as represented in **Scheme-II**.

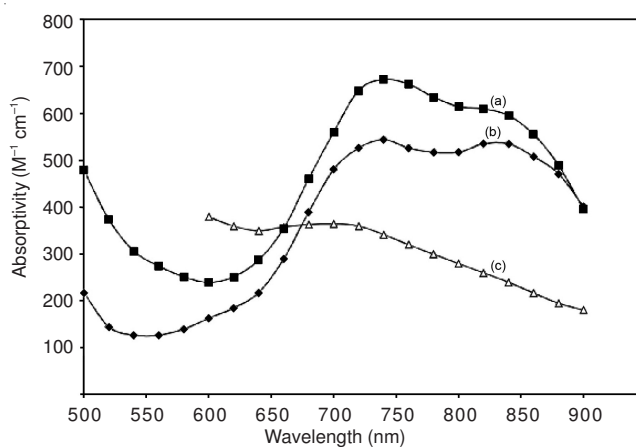
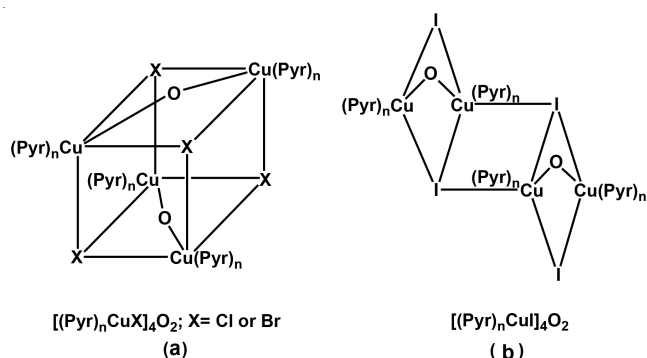


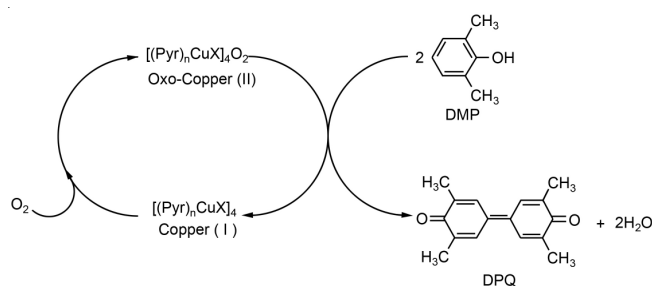
Fig. 1. Electronic spectra of [(Pyr)CuX]₄O₂; (a) X = Cl, (b) X = Br and (c) X = I

The pyrrolidyl hydrogen atom allows association of the tetranuclear copper(I), [(Pyr)_nCuX]₄O₂, with the incoming

dioxygen. Such association is the key for oxidation of $[(\text{Pyr})_n\text{CuI}]_4$ under mild condition, which is not the case for pyridine and *N,N*-diethyl nicotinamide^{8,9} ligands, both of them are less basic and did not have an N-H group.



Scheme-I: Proposed molecular core structure for $[(\text{Pyr})_n\text{CuX}]_4\text{O}_2$; $n = 1$ or 2 , X = Cl, Br and I



Scheme-II: Catalytic cycle for homogeneous oxidative coupling of phenols

The objective of this work is the studying of half of the homogeneous oxidative coupling catalytic cycle for phenol oxidation, which represent the oxidation of copper(I) by dioxygen (**Scheme-II**) and answering the following questions; (a) How does k_{on} ($k_{\text{on}} = Kk_2$) of the oxidation of copper(I) by dioxygen operate in the presence of pyrrolidyl hydrogen? (b) What are the effects of changing the amine/copper ratio from 1:1 to 2:1 on the rate of oxidation of copper(I) by dioxygen? and (c) What is the significance of changing the halo ligand (X = Cl, Br or I) in $[(\text{Pyr})_n\text{CuX}]_4$.

EXPERIMENTAL

Nitrobenzene was distilled under reduced pressure from P_4O_{10} and stored over 4 Å molecular sieves. Methylene chloride was washed with concentrated sulfuric acid, dried over sodium carbonate, refluxed over P_4O_{10} , then distilled and stored over anhydrous carbonate⁹.

High purity dinitrogen gas was deoxygenated by passing through a column of Alfa-DE-OX solid catalyst and dried by passing through a 60-cm column of dehydrated silica gel and 30-cm column of calcium chloride and molecular sieves.

The pyrrolidine (Pyr), (Aldrich) was used as received. Copper(I) halides were prepared as described in literature¹⁰. $[(\text{Pyr})_n\text{CuX}]_4$ and $[(\text{Pyr})_n\text{CuX}]_4\text{O}_2$ ($n = 1$ or 2 , X = Cl, Br or I) were prepared as previously described⁷.

Physical measurements: Electronic spectra of reactants and products in nitrobenzene or methylene chloride were measured with a Shimadzu 160A ultraviolet-visible recording

spectrophotometer or with Beckman DB-G spectrophotometer in matched quartz cells.

The consumption of dioxygen by the nitrobenzene solution of $[(\text{Pyr})_n\text{CuX}]_4$, $n = 1$ or 2 , X = Cl, Br or I, was monitored by standard Warburg manometry¹¹ at room temperature and atmospheric pressure.

For kinetics of oxidation of $[(\text{Pyr})_n\text{CuX}]_4$, $n = 1$ or 2 , X = Cl, Br or I by dioxygen in nitrobenzene or methylene chloride, the rates for the oxidation of $[(\text{Pyr})_n\text{CuX}]_4$ with dioxygen were monitored spectrophotometrically. A Beckman DB-G spectrophotometer (connected to BAS XY-t recorder, which provides pen with maximum speed of 2200 mm/s for the y-axis and 2000 mm/s for the X-axis) and fitted with a cell housing maintained within ± 0.1 °C for the desired temperature.

All reactants were thermostated for at least 20 min before fast injection of dioxygen. The monitoring wavelength was 740 nm for $[(\text{Pyr})_n\text{CuX}]_4\text{O}_2$ formation (Fig. 1).

RESULTS AND DISCUSSION

Kinetics of oxidation of $[(\text{Pyr})_n\text{CuX}]_4$ ($n = 1$ or 2 , X = Cl, Br or I), by dioxygen in aprotic media: Kinetic data are represented for the reactions of dioxygen with excess or equal initial concentrations of $[(\text{Pyr})_n\text{CuX}]_4$ complexes, ($n = 1$ or 2 , X = Cl, Br or I), in a range of aprotic solvents. The reactions are easily monitored spectrophotometrically in the visible region and the rates fall in the conventional time domains. Where possible, wide temperature have been employed to allow the estimation of precise activation parameters.

For excess of $[(\text{Pyr})\text{CuCl}]_4$, first-order plots of $\ln(A_\infty - A_t)/(A_\infty - A_0)$ vs. time, where A_t is the absorbance of $[(\text{Pyr})\text{CuCl}]_4\text{O}_2$ at time t , were linear for at least four half-lives, Fig. 2, indicating that reaction (3) is first order in $[\text{O}_2]$.

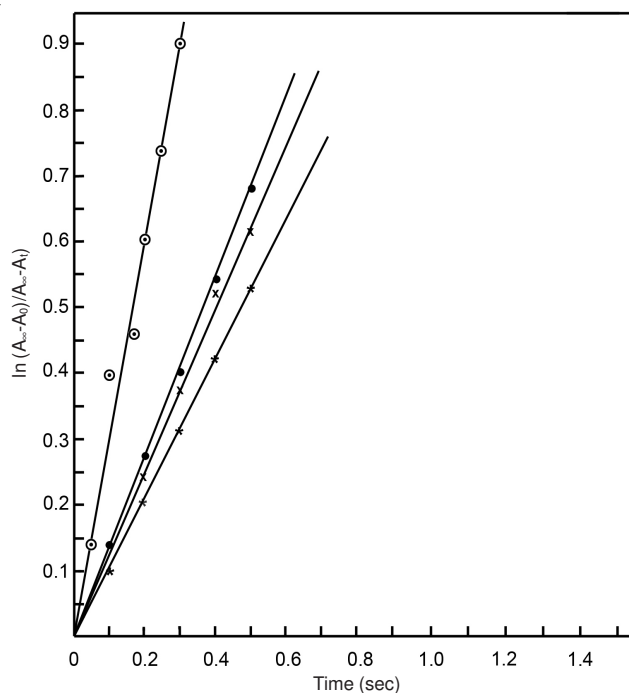


Fig. 2. First-order product formation in the reaction of excess $[(\text{Pyr})\text{CuCl}]_4$ (*), $(4.8 \times 10^{-3} \text{ M})$, (x) $(6.0 \times 10^{-3} \text{ M})$, (^) $(8.0 \times 10^{-3} \text{ M})$, (o) $(14 \times 10^{-3} \text{ M})$ with dioxygen $(4.4 \times 10^{-4} \text{ M})$ in nitrobenzene at 36 °C. Monitoring wavelength is 740 nm

Absorbance extrapolated to zero time correspond to those expected for copper (I) reactant at monitoring wavelength 740 nm, thus providing no evidence for reactant pre-equilibria. The simple first-order rate dependence indicates either that significant concentrations of reaction intermediates are not formed, or that they do not absorb appreciably at 740 nm.

The derived pseudo-first-order rate constant k_{obsd} , were accurately proportional to $[(\text{Pyr})\text{CuCl}]_4$, to give straight line passing through the origin, Fig. 3. Reaction (3, $n = 1$) is thus a second-order process, eq. (4), when $(\text{Pyr})\text{CuCl}_4$ is in excess.

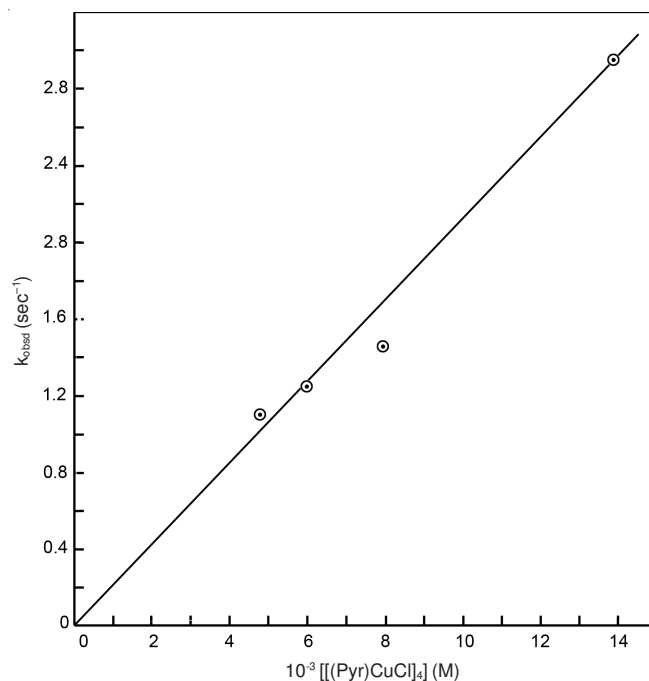


Fig. 3. Dependence of the observed pseudo first order rate constant k_{obsd} on $[(\text{Pyr})\text{CuCl}]_4$ for the reaction with dioxygen in nitrobenzene at 36 °C. Monitoring wavelength is 740 nm

For equal initial concentrations of $[(\text{Pyr})_n\text{CuX}]_4$ ($n = 1$ or 2, $X = \text{Cl}$, Br or I) and dioxygen $[\text{O}_2]$, second order plots of $A_t/(A_\infty - A_t)$ vs. time where A_t is the absorbance of $[(\text{Pyr})_n\text{CuX}]_4\text{O}_2$ at time t , were linear, passing through the origins (Fig. 4), indicating that reaction (3) is a second-order process, eqn. (5). k_{on} obtained from pseudo or equal initial concentration conditions are identical within 3 % for $[(\text{Pyr})\text{CuCl}]_4$ system, Table-1.



Second-order rate constants, k_{on} and their activation parameters [determined from a non linear least-squares fit of the data to eqn. (5), with temperature as an independent variable in nitrobenzene at 740 nm] are listed in Table-1.

Since, the pseudo and equal initial concentrations conditions are agreed for oxidation of $[(\text{Pyr})\text{CuCl}]_4$, the oxidation of $[(\text{Pyr})_n\text{CuX}]_4$ ($n = 1$ or 2 and $X = \text{Cl}$, Br or I) are only studied by slower equal initial concentrations method.

Table-1 reflects that oxidation of $[(\text{Pyr})_n\text{CuX}]_4$, ($n = 1$ or 2 and $X = \text{Cl}$, Br or I) by dioxygen in nitrobenzene are second-order processes (eqn. 5). They also show that the equal initial concentrations method is more convenient than pseudo one, as the former method is more slow.

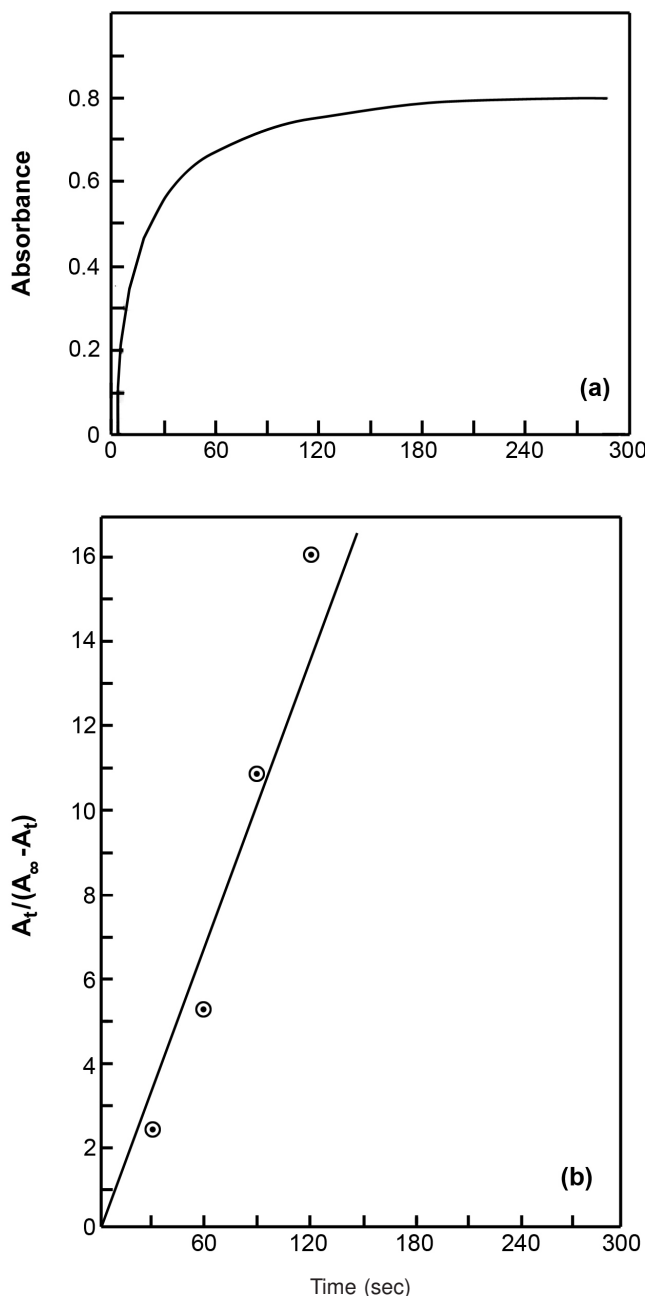
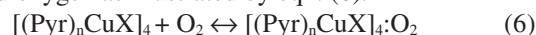


Fig. 4. Second-order plots of equal concentration for the oxidation of $[(\text{Pyr})\text{CuCl}]_4$ (7.3×10^{-4} M) with dioxygen (7.3×10^{-4} M) in nitrobenzene at (○) 30 °C, (×) 36 °C, (⊙) 40 °C, (*) 48 °C, (◆) 60 °C. Monitoring wavelength is 740 nm

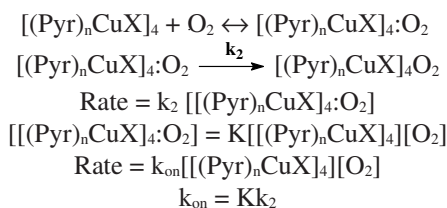
Both activated enthalpies and entropies for $[(\text{Pyr})_n\text{CuX}]_4$ systems have negative values as listed in Table-1. The negative activation enthalpies (ΔH^\ddagger) for the oxidation of $[(\text{Pyr})_n\text{CuX}]_4$, ($n = 1$ or 2 and $X = \text{Cl}$, Br or I) have been observed before in similar works⁵.

Negative ΔH^\ddagger means pre-equilibrium proceeds the rate-determining step. The pre-equilibrium can be represented as an associative interaction between tetranuclear copper (I) and incoming dioxygen as illustrated by eqn. (6).



The very negative activation entropies indicate substantial associative character in the activation process. The magnitude of ΔS^\ddagger are expected for association of two neutral reactant

species to give the activated complex^{4,12,13}. The following mechanism (**Scheme-III**) represents the mechanistic pathway for the oxidation of $[(\text{Pyr})_n\text{CuX}]_4$ ($n = 1$ or 2 , $X = \text{Cl}$, Br or I) by dioxygen in aprotic solvent.



Scheme-III: Mechanism of oxidation of $[(\text{Pyr})_n\text{CuX}]_4$ by dioxygen in aprotic Solvent ($n = 1$ or 2 , $X = \text{Cl}$, Br or I)

k_{on} is the products of the thermodynamic equilibrium constant of the pre-equilibrium, K and rate constant k_2 of the slow step.

TABLE-1 KINETIC DATA FOR OXIDATION OF $f(\text{Pyr})_n\text{CuX}]_4$ COMPLEXES; $n = 1$ OR 2 , $X = \text{Cl}$, Br OR I BY DIOXYGEN IN NITROBENZENE AT 740 nm				
Pyr, n, X	Temp. (°C)	$10^{-3}k_{\text{on}}^{\text{d}}$, $\text{M}^{-1}\text{s}^{-1}$	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger , (cal deg ⁻¹ mol ⁻¹)
Pyr ^(a) , 1, Cl	36	0.210	-	-
Pyr ^(b) , 1, Cl	30	0.240	-11.0 ± 0.5	-84 ± 3
	36	0.220		
	40	0.130		
	50	0.060		
	60	0.050		
Pyr ^(b) , 2, Cl	30	0.440	-15.5 ± 0.5	-98 ± 3
	36	0.240		
	50	0.110		
	60	0.050		
Pyr ^(c) , 1, Cl	28	0.150	-	-
Pyr ^(b) , 1, Br	30	2.900	-9.80 ± 0.5	-75 ± 3
	34	2.100		
	45	1.400		
	60	0.680		
Pyr ^(b) , 2, Br	30	0.950	-4.90 ± 0.5	-61 ± 3
	40	0.760		
	60	0.500		
Pyr ^(b) , 1, I*	16	0.050	-15.0 ± 0.5	-92 ± 3
	20	0.030		
	30	0.020		
Pyr ^(b) , 2, I*	16	0.130	-12.0 ± 0.5	-86 ± 3
	20	0.110		
	25	0.090		
	30	0.060		
Pyr ^(c) , 1, I*	20	0.020	-	-

^aMeasured under pseudo conditions for $[(\text{Pyr})_n\text{CuX}]_4$, $[(\text{Pyr})_n\text{CuX}]_4 = (4.8-14) \times 10^{-3} \text{M}$ and $[\text{O}_2] = 4.4 \times 10^{-4} \text{M}$; ^bMeasured under equal concentrations of both $[(\text{Pyr})_n\text{CuX}]_4$ and dioxygen, $[(\text{Pyr})_n\text{CuX}]_4 = [\text{O}_2] = 7.3 \times 10^{-4} \text{M}$. ^cMeasured under equal concentrations of both $[(\text{Pyr})_n\text{CuX}]_4$ and dioxygen in CH_2Cl_2 , $[(\text{Pyr})_n\text{CuX}]_4 = [\text{O}_2] = 7.3 \times 10^{-4} \text{M}$. ^dUncertainties for k_{on} ca ± 5 % $\text{M}^{-1}\text{s}^{-1}$. *Measured at 500 nm

From the data of Table-1, one can see the following observations: for $n = 1$, on changing X from Cl to Br the rate of oxidation increased by about factor of 12, while for $n = 2$ the rate of oxidation increased by about factor of 2 for the same change. The pyrrolidyl hydrogen and the less electronegativity of Br relative to Cl help the association of incoming

dioxygen with tetranuclear copper(I), *i.e.*, increasing the equilibrium constant K , Scheme (3), such effect getting less for $n = 2$, because of steric effect of higher coordination number around copper(I), which hinder the association of incoming dioxygen.

For the same halogen on changing the number of pyrrolidine around copper (I) from $n = 1$ to $n = 2$, k_{on} increased by factor of two for chloro-one while decrease by factor of three for bromo-analog. Therefore, for X equal chloro, pyrrolidyl hydrogens are more pronounced on the equilibrium constant K , while for bromo-analog, steric effect hinder the association of incoming dioxygen.

The rate constants for oxidation of both $[(\text{Pyr})\text{CuX}]_4$, $X = \text{Cl}$ or I (Table-1), decrease only by about 30 % on changing the solvent from dipolar aprotic solvent, nitrobenzene, to non polar aprotic solvent, methylene chloride, Fig. 5, suggesting that electron transfer from copper(I) to dioxygen, which produces a polar state is not the rate determining step.

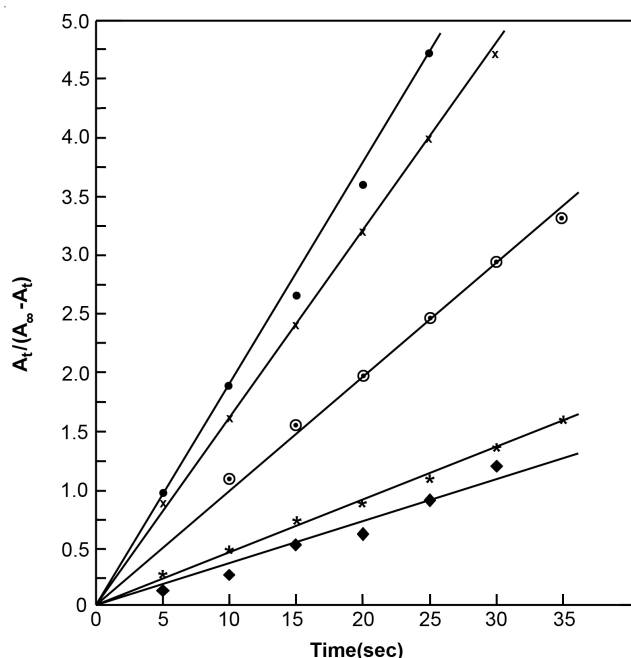
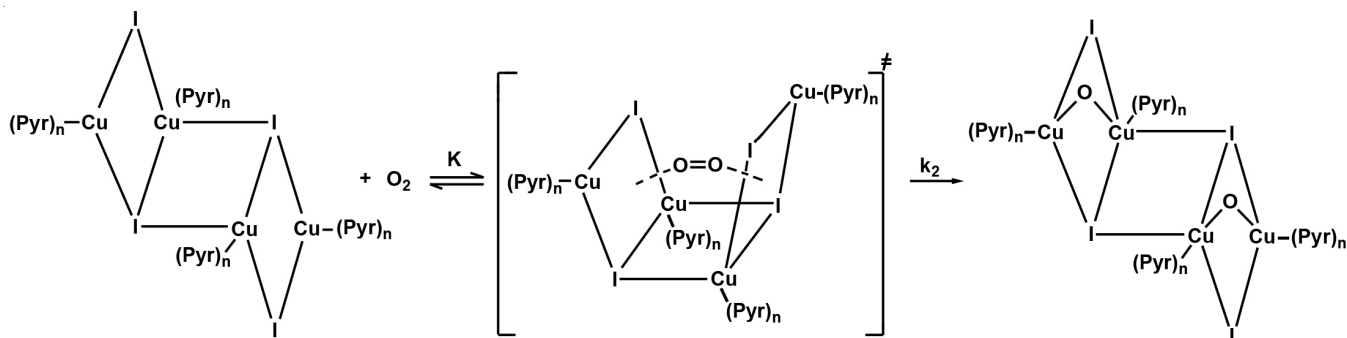


Fig. 5. (a) Absorbance-time data for equal concentration of oxidation of $[(\text{Pyr})\text{CuCl}]_4$ ($7.3 \times 10^{-4} \text{M}$) with dioxygen ($7.3 \times 10^{-4} \text{M}$) in methylene chloride at 28 °C. Monitoring wavelength is 740 nm. (b) second order plot of $A_t/(A_\infty - A_t)$ vs. time for the data in the upper panel

On changing X from Cl or Br to I , the k_{on} decrease dramatically and more negative ΔH^\ddagger and ΔS^\ddagger are observed, Table-1. Such observation supports the spectroscopic conclusion of step structure for $[(\text{Pyr})_n\text{CuI}]_4\text{O}_2$, **Scheme-Ib**) and suggests the structure of the activated complex as dioxygen associates two faces before O-O bond breaking (**Scheme-IV**).

Including similar work for oxidation of tetranuclear cubane copper(I) complexes^{5,9,14} by dioxygen in aprotic media, one can conclude that, the values of second-order rate of oxidation, k_{on} (**Scheme-III**) are very sensitive to the nature and number of ligands around copper(I) in $[(\text{L})_n\text{CuX}]_4$ ($\text{L} = \text{pyridine (Py)}$, *N,N*-diethyl nicotinamide (DENC) piperidine (Pip) or pyrrolidine (Pyr); $n = 1$ or 2 and $X = \text{Cl}$ or Br). Both piperidine (Pip) and pyrrolidine (Pyr), ($\text{pK}_b = 2.80$ and 2.73



Scheme-IV: Proposed structure for activated complex as dioxygen associates two faces

respectively), are more basic than pyridine (Py) ($pK_b = 8.8$) and its derivative *N,N*-diethyl nicotinamide (DENC). In addition, piperidine and pyrrolidine have free hydrogen atom (N-H), which helped the assembling of O_2 through hydrogen bonding.

Therefore, the negative enthalpy of activation ΔH^\ddagger indicates the enhancement of thermodynamic equilibrium constant (K) over the kinetic rate constant (k_2) in $k_{on} = Kk_2$.

A plot of ΔH^\ddagger vs. ΔS^\ddagger (Fig. 6), correlates quite well the data for aprotic oxidation of $[LCuX]_4$ (L = Py, *N,N*-diethyl nicotinamide, Pip and Pyr, X = Cl or Br) by dioxygen. Such correlation supports (Scheme-III) as a common mechanism.

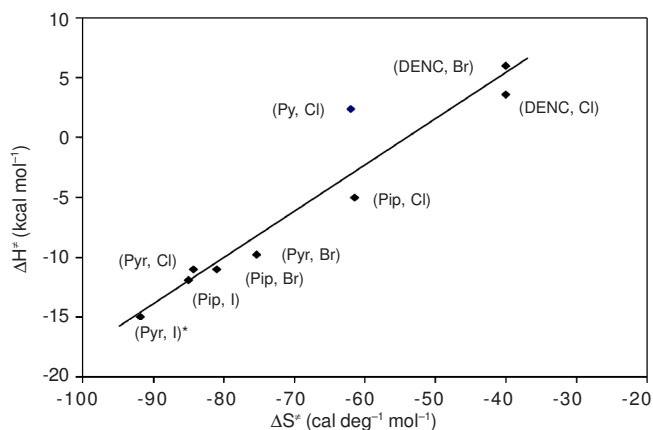


Fig. 6. Plot of ΔH^\ddagger vs. ΔS^\ddagger for the reaction of $[LCuX]_4$ with dioxygen in nitrobenzene where X = Cl, Br and I, L = Pip, Py, DENC and Pyr

Conclusion

Exothermic oxidation of $[(Pyr)_nCuX]_4$ system is promoted by high basicity of pyrrolidine and pyrrolidyl hydrogen, which are behind the pronouncing of pre-equilibrium K.

For $[(Pyr)_nCuX]_4$ systems, one can expect the lowering of electronegativity of X from Cl to I will helps the association

of pyrrolidyl hydrogen with incoming dioxygen and increasing the pre-equilibrium K, Scheme-III) as in case of $[(Pip)CuX]_4$ system⁵.

However, the dramatic decrease of k_{on} and more negative ΔH^\ddagger and ΔS^\ddagger , support the step structure when X = I in $[(Pyr)CuX]_4$, Scheme-IV, which has been concluded by spectroscopically⁷.

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