the effect of the barrier on the association reaction. In a similar manner, the present results for CH + $D_2$ yield information on the dynamics of the association reaction for this system. In the BH system, no onset of the addition–elimination channel could be observed as the abstraction reaction is substantially more endothermic than in the present case.

### Summary

The rate coefficient for the reaction of CH with $D_2$ decreases from 298 to 1260 K. A pressure dependence study showed the CH disappearance rate to be invariant with total pressure at room temperature. Isotope exchange provides near thermoneutral product pathways for loss of CH following formation of a $CHD_2^\dagger$ complex. The CH disappearance rate is therefore directly proportional to the association rate to form $CHD_2^\dagger$. The observed negative temperature dependence confirms theoretical results[19] indicating the isotopically related association reaction leading to $CH_3^\dagger$ proceeds with no entrance channel barrier.

The addition–elimination product channel for this reaction has been investigated with a study of the temperature dependence of the CD + $D_2$ reaction. The activation energy for the addition–elimination channel is shown to be approximately equal to the reaction enthalpy. This confirms the findings of Aoyagi et al.[18] that there is no barrier to the $CH_2$ + H reaction. Assuming the reaction thermochemistry controls the product branching ratio, the addition–elimination reaction is expected to dominate above 2100 K.

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# Determination of the Volume of Activation of the Key Reaction Steps in the Oxidation of Phenanthroline–Copper(I) by Molecular Oxygen

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Using the high-pressure pulse radiolysis technique, we have shown that the oxidation of $(phen)_2Cu^I$ (phen = 1,10-phenanthroline) by molecular oxygen proceeds via a transient in which a copper–oxygen bond is formed, i.e., via $Cu^I–O_2$ as an intermediate. The volume of activation measured for this process is $-22 \pm 2$ cm$^3$ mol$^{-1}$. When high concentrations of $(phen)_2Cu^{II}$ are present in the solution, this transient reacts with another $(phen)_2Cu^I$ yielding $(phen)_2Cu^{II}$ and $H_2O_2$. If the latter reaction involves the formation of $Cu^IO_2Cu^I$ as an intermediate, it is produced with a rate constant close to the diffusion-controlled limit. In the presence of low concentrations of $(phen)_2Cu^{II}$, $Cu^I–O_2$ decomposes to $(phen)_2Cu^{II}$ and $O_2^-$, where subsequently $O_2^-$ reacts with another $(phen)_2Cu^I$ to produce $(phen)_2Cu^{II}$ and $H_2O_2$.

## Introduction

Basic information on the reaction of copper(I) complexes with molecular oxygen is of great importance for understanding the pathways of oxygen in copper-catalyzed autoxidation reactions in both chemical and biological systems.[1-4] A study of the mechanism of the oxidation of $Cu^I$ complexes by molecular oxygen may enhance the understanding of the mechanism by which the copper-based oxygen-transport system hemocyanin functions, as well as contribute to the understanding of the oxidation of transition metal ions by $O_2$.

The rate of the autoxidation of cuprous ions was found to be influenced by the ligand environment. The reaction mechanism has been investigated in detail with many nitrogen-containing ligands.[4-10] However, notwithstanding the importance of the relevance of these processes, the mechanisms of these reactions are far from being well understood. For instance, different values of the reaction order with respect to $Cu^I$ (where $Cu^I$ denotes a monovalent copper complex) have been reported,[5,7,8,10] and though the formation of a $Cu^I–O_2$ adduct was postulated, experimental evidence for its existance was weak.[4-10] The kinetic data in many

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of these studies suggest two possible autoxidation mechanisms consistent with the observed rate law. The first mechanism involves a two-electron reduction of $O_2$ to $H_2O_2$ via

$$\mathrm{Cu^I} + \mathrm{O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cu^I{-}O_2} \qquad (1)$$

$$\mathrm{Cu^I{-}O_2} + \mathrm{Cu^I} \xrightarrow[k_2]{2\mathrm{H^+}} 2\mathrm{Cu^{II}} + \mathrm{H_2O_2} \qquad (2)$$

The second mechanism involves the stepwise reduction of $O_2$ by $Cu^I$ to form $O_2^-$ as an intermediate via

$$\mathrm{Cu^I} + \mathrm{O_2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Cu^{II}} + \mathrm{O_2^-} \qquad (3)$$

$$\mathrm{Cu^I} + \mathrm{O_2^-} \xrightarrow[k_4]{2\mathrm{H^+}} \mathrm{Cu^{II}} + \mathrm{H_2O_2} \qquad (4)$$

The one-electron reduction of $O_2$ to $O_2^-$ seemed to be thermodynamically an unfavorable process, since some of the authors took wrong values for the redox potential of the $O_2^-/O_2$ couple.[6,7] Goldstein and Czapski,[8,10] using the pulse radiolysis technique, have shown that the above outlined mechanisms can account for the reduction of molecular oxygen by cuprous complexes of 1,10-phenanthroline (phen) and some other substituted phenanthrolines as well as bipyridine. They have demonstrated that at initial high concentrations of $Cu^{II}$ the first mechanism is dominant, whereas at low concentrations of $Cu^{II}$, the first mechanism can be neglected, and the second mechanism is the dominant one.[8,10] The formation of $O_2^-$ as an intermediate has been demonstrated by the addition of bovine superoxide dismutase (SOD), which catalyzes $O_2^-$ dismutation into $O_2$ and $H_2O_2$, to the reaction mixture. The presence of SOD accelerated the rate of the oxidation of $(phen)_2Cu^I$ by $O_2$ and changed the kinetics of the reaction, as in such a case only the forward of reaction 3 takes place.[8,10]

Volumes of activation have in general been shown to possess a high mechanistic discrimination ability in thermal and photochemical reactions of inorganic and organometallic complexes.[11-13] We have therefore decided to measure with the aid of a high-pressure pulse radiolysis technique the volume of activation for the oxidation of $(phen)_2Cu^I$ by $O_2$ at high $[Cu^{II}]_0$, where mainly the first mechanism operates, and at low $[Cu^{II}]_0$ in the presence of SOD, where only reaction 3 accounts for the oxidation process. Our aim was to find out whether an additional intermediate is formed in reaction 2 of the kind $Cu^IO_2Cu^I$ as suggested earlier[14,15] and whether reaction 3 is an outer-sphere electron-transfer reaction or whether it involves the formation of $Cu^I{-}O_2$ as an intermediate. We have chosen to study this system as the mechanism of this reaction has been studied in detail earlier, and all the relevant rate constants are available at ambient pressure.[8] In addition, $(phen)_2Cu^I$ absorbs highly in the visible region ($\epsilon_{435} = 7800$ $M^{-1}$ $cm^{-1}$ [8]), which enabled us to easily follow the change in its absorbance with the high-pressure system, which contains a special optical cell, with a short optical path length of 1 cm, which is placed in a high-pressure container that blocks most of the ionizing radiation.

## Experimental Section

All chemicals were of analytical grade and were used as received: 1,10-phenanthroline (Fluka), cupric sulfate, sodium formate, monosodium and disodium phosphate (Merck), bovine SOD (Sigma). All solutions were prepared with distilled water that was passed through a Millipore ultrapurification system. Solutions for irradiation were prepared by mixing 2.2 equiv of the ligand with 1 equiv of copper sulfate in oxygenated solutions containing 50 mM formate at pH 6.8 (1 mM phosphate buffer). The experiments were carried out at 17 °C.

Pulse radiolysis experiments were carried out with a Varian 7715 linear accelerator at the Hebrew University of Jerusalem with a 200-mA current of 5-MeV electrons using a transportable high-pressure unit complete with a four-window pressure cell.[16] Irradiations were done in a 1-cm pillbox optical cell made of suprasil.[17] This cell was positioned close to a thin stainless steel window of the modified high-pressure cell. Water was used as the pressurizing medium, and experiments were performed up to 1500 atm pressure. A 150-W Xe–Hg lamp was used as the light source. The detection system included a Bausch & Lomb grating double monochromator (Model D330/D331 Mk.II) and an IP28 photomultiplier. The signal was transferred through a Sony/Textronix 390AD programmable digitizer to a micro PDP-11/24 computer, which operated the whole pulse radiolysis system.

On pulsing $O_2$-saturated solutions containing formate, the following reactions take place at ambient pressure:

$$\mathrm{H_2O} \rightsquigarrow \mathrm{e_{aq}^-},\ \mathrm{OH^\bullet},\ \mathrm{H^\bullet},\ \mathrm{H_2O_2},\ \mathrm{H_2},\ \mathrm{H_3O^+} \qquad (5)$$

$$\mathrm{e_{aq}^-} + \mathrm{O_2} \rightarrow \mathrm{O_2^-} \qquad k_6 = 2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ (\text{ref } 18) \qquad (6)$$

$$\begin{gathered}\mathrm{OH^\bullet} + \mathrm{HCO_2^-} \rightarrow \mathrm{H_2O} + \mathrm{CO_2^-} \\ k_7 = 3.5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ (\text{ref } 18)\end{gathered} \qquad (7)$$

$$\begin{gathered}\mathrm{CO_2^-} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{O_2^-} \\ k_8 = 2.4 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ (\text{ref } 19)\end{gathered} \qquad (8)$$

$$\mathrm{H^\bullet} + \mathrm{O_2} \rightarrow \mathrm{HO_2^\bullet} \qquad k_9 = 2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ (\text{ref } 18) \qquad (9)$$

$$\mathrm{HO_2^\bullet} \rightleftharpoons \mathrm{H^+} + \mathrm{O_2^-} \qquad \mathrm{p}K_\mathrm{a} = 4.7\ (\text{ref } 20) \qquad (10)$$

Because of the high rate constants of these reactions, all the primary radicals are converted into $O_2^-$ within the duration of the pulse, which subsequently reduces $(phen)_2Cu^{II}$ via

$$\begin{gathered}\mathrm{(phen)_2Cu^{II}} + \mathrm{O_2^-} \rightarrow \mathrm{(phen)_2Cu^I} + \mathrm{O_2} \\ k_{11} = 1.9 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ (\text{ref } 8)\end{gathered} \qquad (11)$$

The change in the absorbance was followed at 435 nm, where $(phen)_2Cu^I$ absorbs highly by using $\epsilon = 7800$ $M^{-1}$ $cm^{-1}$.[8] The initial concentration of $(phen)_2Cu^I$ thus formed was about 3 μM.

## Results

Oxygen-saturated solutions ($1.25 \times 10^{-3}$ M) containing $5 \times 10^{-4}$ M $(phen)_2Cu^{II}$ and 0.05 M formate at pH 6.8 were irradiated by a 1.5-μs electron pulse. The formation of $(phen)_2Cu^I$ was observed, being completed 5 μs after the end of the pulse. The absorbance of $(phen)_2Cu^I$ disappeared in a process obeying a second-order rate law. The rate of this process was measured at ambient and 500, 1000, and 1500 atm pressure. In Figure 1a,b typical kinetic plots (including second-order plots as inserts) are given at 1 and 1500 atm, respectively. At each pressure at least five experiments were performed, and the observed rate constant is an average of the measured rate constants. The experimental deviation was less than 5%. The observed second-order rate constant increased as the pressure increased, and a plot of $\ln k_{obs}$ as a function of pressure yielded a straight line (Figure 2). From the slope of the line a volume of activation of $-20 \pm 2$ $cm^3$ $mol^{-1}$ was obtained.

To measure the rate of the reaction at low $(phen)_2Cu^{II}$ concentrations, experiments with SOD added to the solutions were

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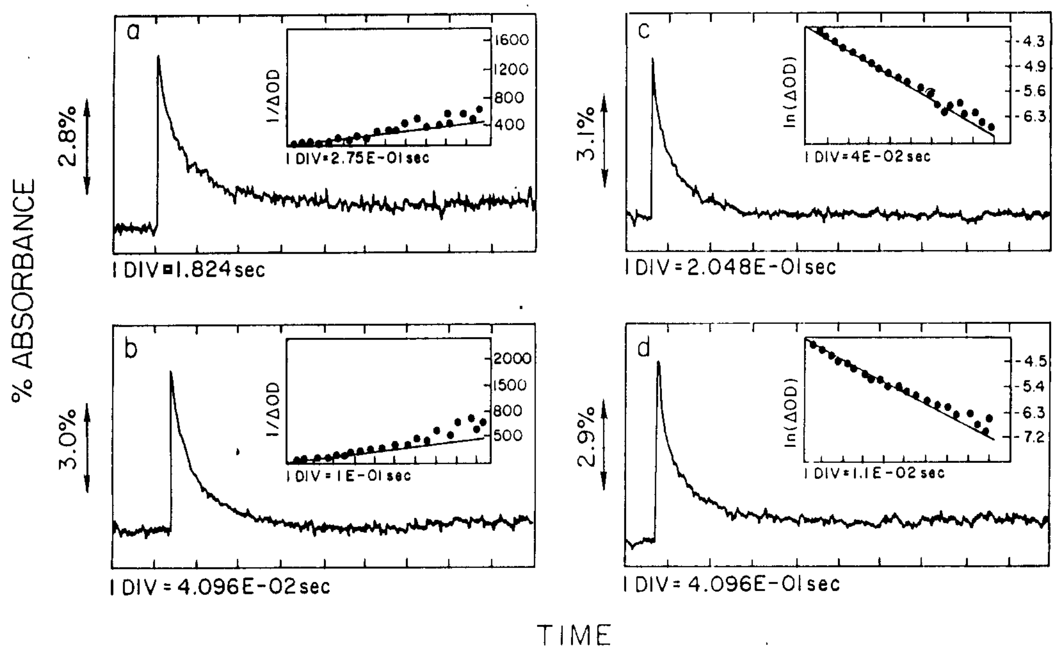

**Figure 1.** The decay of the absorbance of $(phen)_2Cu^I$ in oxygenated solutions at pH 6.8 (1 mM phosphate buffer) containing 0.05 M formate: (a) $5 \times 10^{-4}$ M $(phen)_2Cu^{II}$, 1 atm; (b) $5 \times 10^{-4}$ M $(phen)_2Cu^{II}$, 1500 atm; (c) $2 \times 10^{-5}$ M $(phen)_2Cu^{II}$, 6.2 μM SOD, 1 atm; (d) $2 \times 10^{-5}$ M $(phen)_2Cu^{II}$, 6.2 μM SOD, 1500 atm.

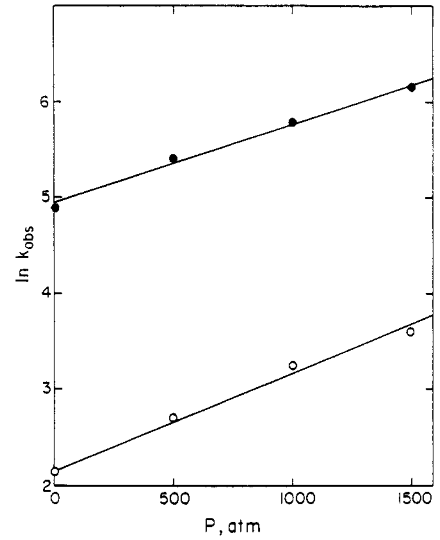

**Figure 2.** The dependence of ln $k_{obs}$ on pressure: (●) $5 \times 10^{-4}$ M $(phen)_2Cu^{II}$; (○) $2 \times 10^{-5}$ M $(phen)_2Cu^{II}$, 6.2 μM SOD. Solutions were oxygen saturated at pH 6.8 (1 mM phosphate buffer) and contained 0.05 M formate.

performed. Relatively low initial concentrations of $2 \times 10^{-5}$ M $(phen)_2Cu^{II}$ and 6.2 μM SOD were used. In this case the formation of $(phen)_2Cu^I$ was completed within 100 μs after the pulse. The decay of the absorbance changed and obeyed a first-order rate law. Typical kinetic traces (including first-order plots as inserts) are given in Figure 1c,d at 1 and 1500 atm, respectively. The observed first-order rate constant, measured at 1, 500, 1000, and 1500 atm, increased as the pressure increased, and a plot of ln $k_{obs}$ as a function of pressure yielded a straight line (Figure 2). From the slope of the line a volume of activation of −24 ± 2 $cm^3$ $mol^{-1}$ was obtained.

## Discussion

It has already been demonstrated that at ambient pressure the oxidation of $(phen)_2Cu^I$ by molecular oxygen involves both a stepwise one-electron reduction (reactions 1 and 2) and a two-electron reduction of $O_2$ (reactions 3 and 4).[8] The rate law for these processes was found to be first order with respect to $[O_2]$ and second order with respect to $[(phen)_2Cu^I]$, and the rate depended inversely on $[(phen)_2Cu^{II}]_0$.[8] Assuming a steady-state approximation for $[O_2^-]$ and $[Cu^I{-}O_2]$, rate eq 12 was obtained.

$$-d[Cu^I]/dt = \{2k_1k_2/(k_{-1} + k_2[Cu^I]) + 2k_3k_4/k_{-3}[Cu^{II}]_0\}[O_2][Cu^I]^2 \quad (12)$$

At relatively high concentrations of $[Cu(II)]_0$, the second term in eq 12 can be neglected, and rate eq 12 is reduced to rate eq 13. As the rate of the decay of $(phen)_2Cu^I$ obeyed a second-order

$$-d[Cu^I]dt = \{2k_1k_2/(k_{-1} + k_2[Cu^I])\}[O_2][Cu^I]^2 \quad (13)$$

rate law, it was assumed that $k_{-1} \gg k_2[Cu^I]$, and

$$k_{obs} = 2k_1k_2[O_2]/k_{-1} \quad (14)$$

According to this mechanism the volume of activation is given by

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}(k_1) + \Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_{-1}) = \Delta\bar{V}(K_1) + \Delta V^{\ddagger}(k_2) \quad (15)$$

The volume of activation of reaction 1 is negative due to bond formation, whereas that of reaction −1 is positive. If reaction 2 also proceeds through bond formation or if its rate is diffusion controlled such that it will not vary significantly with pressure, then the overall volume of activation of this process is negative. Indeed, the observed second-order rate constant increased significantly with increasing pressure, and from the slope of the line in Figure 2 a value of $\Delta V^{\ddagger} = -(20 \pm 2)$ $cm^3$ $mol^{-1}$ was obtained.

At low $[Cu^{II}]_0$, the first term in eq 12 can be neglected, and in the presence of SOD rate eq 16 is obtained.[8]

$$-d[Cu^I]/dt = \{k_3k_{cat}[SOD][O_2]/(k_{-3}[Cu^{II}]_0 + k_{cat}[SOD])\}[Cu^I] \quad (16)$$

Since $k_{cat} = (2-3) \times 10^9$ $M^{-1}$ $s^{-1}$[21] and $k_{-3} \equiv k_{11} = 1.9 \times 10^9$ $M^{-1}$ $s^{-1}$[8] are rate constants of reactions that are diffusion controlled, they will not vary with pressure since the viscosity of water is independent of pressure over the investigated range, and the volume of activation measured under these conditions is just $\Delta V^{\ddagger}(k_3)$. The observed first-order rate constant increased with increasing pressure, and the volume of activation obtained from Figure 2 is −24 ± 2 $cm^3$ $mol^{-1}$. This value points toward a bond formation between $Cu^I$ and $O_2$ and cannot be accounted for in terms of an outer-sphere electron-transfer reaction in which a 2+ and 1− species are formed, i.e., only in terms of changes in the

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electrostriction due to charge creation. This would mean that reaction 3 must proceed via bond formation, i.e., via

$$Cu^{I} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu^{I}\text{–}O_2 \xrightarrow{k_3'} Cu^{II} + O_2^- \qquad (17)$$

where $k_3 = k_1k_3'/k_{-1}$, and

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}(k_1) - \Delta V^{\ddagger}(k_{-1}) + \Delta V^{\ddagger}(k_3') = \Delta\bar{V}(K_1) + \Delta V^{\ddagger}(k_3') \qquad (18)$$

The observed $\Delta V^{\ddagger}$ will mainly represent $\Delta\bar{V}(K_1)$, whose average value is $-22$ cm$^3$ mol$^{-1}$, since reaction 3′ involves a bond breakage ($+\Delta V^{\ddagger}$) accompanied by a charge creation ($-\Delta V^{\ddagger}$), and therefore $\Delta V^{\ddagger}(k_3')$ is expected to be close to zero. Recently, a similar value of ca. $-20$ cm$^3$ mol$^{-1}$ was reported in the case of myoglobin for the reaction $Mb + O_2 \rightleftharpoons MbO_2$.[22]

Thus, if $\Delta\bar{V}(K_1) = \Delta V^{\ddagger}(k_1) - \Delta V^{\ddagger}(k_{-1})$ is ca. $-22$ cm$^3$ mol$^{-1}$, it follows from eq 15 that $\Delta V^{\ddagger}(k_2)$ must also be close to zero. This means that reaction 2 either is diffusion controlled (no pressure dependence in water) or involves a process that is not accompanied by a significant volume change. The mechanism of reaction 2 can be described via the formation of $(Cu^+O_2^-)$ as an intermediate:

$$CuO_2^+ + Cu^+ \rightarrow Cu^{2+} + (Cu^+O_2^-) \qquad (19)$$

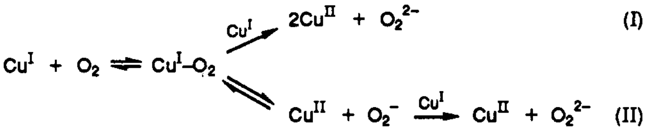
where formally no charge creation occurs. Reaction 2 may also proceed via the formation of $Cu^{I}O_2Cu^{I}$ as an intermediate where

$$Cu^{I}O_2 + Cu^{I} \rightarrow Cu^{I}O_2Cu^{I} \qquad (20)$$

If $Cu^{I}O_2Cu^{I}$ is formed, it must be produced via a diffusion-controlled process, otherwise one would expect a volume collapse due to a bond formation. Nevertheless, reaction 2 is not elementary and occurs probably through an intermediate. A binuclear complex with a peroxide bridge is very unstable and hydrolizes rapidly in aqueous solutions. Probably the rate of this dimer formation is limited by the lability of the $Cu^{I}$ coordination sphere and is characterized by a rate constant close to the diffusion-controlled limit.[23] Thus, as it has been found that $k_1k_2/k_{-1} = (2.9 \pm 0.3) \times 10^8$ M$^{-1}$ s$^{-1}$,[8] if we assume that $k_2 = 1 \times 10^9$ M$^{-1}$ s$^{-1}$, then $K_1 \leq 0.3$ M$^{-1}$. A similar value ($K_1 = 0.1$ M$^{-1}$) has been found in the case of bipyridine–$Cu^{I}$ and $O_2$, where it was also assumed that reaction 2 proceeds via the formation of a dimer with a rate constant of about $1 \times 10^9$ M$^{-1}$ s$^{-1}$.[24]

## Conclusions

By measurement of the volume of activation of the reduction of molecular oxygen by $(phen)_2Cu^{I}$, it was possible to show that under all experimental conditions the reaction proceeds via the formation of an intermediate with a copper–oxygen bond, i.e., via $Cu^{I}$–$O_2$. Depending on the concentration of $(phen)_2Cu^{II}$ present in the solutions, this transient may either react with another $(phen)_2Cu^{I}$ or may decompose to $(phen)_2Cu^{II}$ and $O_2^-$ (eq I and II).



On the basis of the reported volume of activation, the formation of $Cu^{I}O_2Cu^{I}$ via pathway I cannot be demonstrated. If this intermediate is formed, it must be produced with a rate constant approaching the diffusion-controlled limit.

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**Registry No.** $(phen)_2Cu^+$, 17378-82-4; $O_2$, 7782-44-7.

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# Electron-Transfer Kinetics and Ternary Equilibria of the $NO_2^+/NO_2/N_2O_4$ System by Transient Electrochemistry

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The reversible redox potential is established for the $NO_2^+/NO_2$ couple by the cyclic voltammetric (CV) examination of the reduction of the nitronium ion as well as the microscopic reverse oxidation of nitrogen dioxide. The facile association of $NO_2$ and dissociation of $N_2O_4$ are specifically included in the electrode kinetics by the successful computer simulation of the cyclic voltammograms at relatively slow and fast CV scan rates. The kinetics of the $N_2O_4$ dissociation ($k_1$) and $NO_2$ association ($k_2$) are determined with the aid of single-step chronoamperometry by developing the theoretical working curves based on the CE(mono) mechanism in Scheme II. The strong dependence of the redox potential on the medium is associated with significant $NO_2^+$ coordination, as shown by the linear correlation with Gutmann's donor number of the solvent. The heterogeneous rate constant ($k_s$) for electron transfer to $NO_2^+$ is found to be faster than $k_s$ for $NO^+$, despite a significantly enhanced value of the intrinsic reorganization energy of $NO_2^+$ compared to $NO^+$ for outer-sphere electron transfer based on the Marcus model.

## Introduction

Oxidation–reduction bears an important relationship to the chemical reactivity of the various nitrogen oxides.[1] Among these, nitric oxide and nitrogen dioxide are particularly ubiquitous and especially relevant to atmospheric contamination.[2] The estab-

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