J. Phys. Chem. A **2003,** *107,* 6345−6350

ARTICLES

Structure and Dynamics of Bis(triphenylphosphine)-3,6-di-*tert*-butyl-*o*-semiquinone Radical Anion Complexes of Ag^+ and Cu^+

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Received: March 10, 2003; In Final Form: May 28, 2003

Complexes of Ag^+ and Cu^+ with 3,6-di-*tert*-butyl-*o*-semiquinone radical anion ($SQ^{\bullet-}$) and two triphenylphosphine (PPh_3) ligands have been investigated by electron paramagnetic resonance (EPR) in organic solvents. High-temperature EPR spectra of the Ag^+ and Cu^+ complexes contain lines of hyperfine splittings due to two equivalent ^1H nuclei in the 4,5-positions of the aromatic ring of the $SQ^{\bullet-}$ ligand, two equivalent ^{31}P nuclei from the two PPh_3 ligands, and $^{107,109}Ag$ and $^{63,65}Cu$ nuclear isotopes, respectively. On the basis of the temperature dependence of the ^{31}P hyperfine interaction constant $a(^{31}P)$, the structure of the Ag^+ complex at low temperature was determined to be planar, while at higher temperatures the increase in the values of $a(^{31}P)$ shows that phosphorus atoms of the two PPh_3 ligands move out of the π-plane of the $SQ^{\bullet-}$ ligand. EPR spectra of the Ag^+ complex with variable temperature exhibit alternating line width effect in hyperfine splitting due to the two aromatic protons in the $SQ^{\bullet-}$ ligand. At low temperatures these two protons become nonequivalent. This effect reveals a dynamic charge redistribution within Ag^+ and two oxygen atoms of the $SQ^{\bullet-}$ ligand. In the Cu^+ complex, we have found a temperature-independent symmetric charge distribution within two oxygen atoms of the radical anion and Cu^+, but different positions of the two PPh_3 ligands at low temperatures. EPR spectra of the Cu^+ complex at variable temperature reveal the dynamic exchange in the positions of PPh_3 ligands. The rates of this process are on the order of solvent reorientation frequencies, while intramolecular electron exchange rates in the Ag^+ complex are about 2 orders of magnitude lower. The rate of the electron exchange reaction dramatically decreases in viscous mineral oil, which shows that the intramolecular charge redistribution reaction is controlled by nonpolar solvent dynamics.

Introduction

o-Quinones are very interesting molecules for organometallic chemistry, inorganic chemistry, physical chemistry, and materials chemistry research due to their ability to form chelate metal complexes and exist in different oxidation states, including the reduced form, *o*-semiquinone radical anions.[1−9] The ability of *o*-quinones to dissolve metallic silver and copper in organic solvents in the presence of phosphine donors was demonstrated in ref 10. The resulting Ag(I) and Cu(I) complexes with *o*-semiquinone radical anion ligand can also be obtained by the exchange reaction of sodium *o*-semiquinone with Ag(I) trifluoroacetate and Cu(I) chloride, respectively.[10] Under certain conditions, *o*-semiquinone complexes of silver and copper can release the metal atom, which makes the process potentially suitable for metal deposition applications. In a recent study, the surface-enhanced Raman scattering observation of a *p*-semiquinone radical anion complex with silver nanoparticles was reported.[11] This study triggered our interest in the structural details of previously reported silver and copper complexes with *o*-semiquinone ligands, since in contrast to para isomers, *o*-semiquinone radical anions as chelating ligands can form more stable and spectroscopically more informative metal complexes. These details may have further impact on the understanding and development of new silver−quinone-based complexes and nanostructures.

In ref 10, silver and copper complexes, $SQ^{\bullet-}Ag^+(PPh_3)_2$ and $SQ^{\bullet-}Cu^+(PPh_3)_2$ ($SQ^{\bullet-}$ = 3,6-di-*tert*-butyl-*o*-semiquinone radical anion), with two triphenylphosphine (PPh_3) ligands, were characterized in solutions by electron paramagnetic resonance (EPR) spectroscopy. EPR spectral parameters of the complexes were obtained at ambient temperatures, and no analyses on the possible structure and dynamics of these complexes were reported. In our previous research, the $SQ^{\bullet-}$ radical anion has been used as a paramagnetic ligand to probe the structure,

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10.1021/jp030315b CCC: \$25.00

molecular dynamics, and elementary reaction kinetics of metal complexes and organoelement radicals.[12−16] In ref 16, we investigated the relationship between intramolecular and reorientation dynamics of the bis(triphenylphosphine)-3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-semiquinone radical anion complex of copper, $(MeO)_2SQ^{\bullet-}Cu^+(PPh_3)_2$. The use of two methoxy (MeO) radicals in the 4,5-positions of the aromatic ring of the radical anion ligand provided relatively simple EPR spectra, with no additional hyperfine splitting from this ligand, and allowed us to concentrate our research on the reorganization dynamics of the coordination sphere of the complex due to neutral PPh_3 ligands.

The purpose of the present work is to structurally characterize the complexes $SQ^{\bullet-}Ag^+(PPh_3)_2$ and $SQ^{\bullet-}Cu^+(PPh_3)_2$ and study their solution dynamics by EPR spectroscopy. Along with the hyperfine interaction due to central metal ions and phosphorus atoms, we specifically intend to analyze the hyperfine interaction due to protons in the 4,5-positions of the aromatic ring of the $SQ^{\bullet-}$ ligand, and gain information on charge redistribution dynamics in these complexes and its relation to entire coordination sphere dynamics and solvent reorganization.

Experimental Section

The complexes $SQ^{\bullet-}Ag^+(PPh_3)_2$ and $SQ^{\bullet-}Cu^+(PPh_3)_2$ were obtained by the method described in ref 10. The concentration of the paramagnetic complexes in solution never exceeded 10^{-4} M, to exclude concentration effects on line broadening. Solutions of the complexes were prepared in diethyl ether, toluene, pentane, and mineral oil and then placed in quartz EPR tubes and deoxygenated at 10^{-2} atm. EPR spectra were recorded with a Bruker EMX spectrometer operating at 9.6 GHz of microwave frequency, 100 kHz modulation frequency,and 2 mW microwave power. For EPR spectra in liquid solutions, we used 0.05 G modulation amplitude, which is far below the lowest line width of 0.3 G observed for individual line components at high temperatures. For anisotropic EPR spectra in frozen solutions at 77 K, individual line widths were greater than 2 G, so that 0.5 G modulation amplitude was used to enhance spectrum intensities. EPR measurements at variable temperatures were performed using a Bruker BVT 3000 liquid nitrogen temperature control system.

Results and Discussion

In Figure 1 we present EPR spectra of the complex $SQ^{\bullet-}Ag^+(PPh_3)_2$ at different temperatures in toluene. At high temperatures ($T \geq 300$ K), the EPR spectrum shows splittings due to hyperfine interaction of the unpaired electron with two equivalent ^{31}P nuclei, $a(^{31}P) = 5.25$ G, two equivalent protons in the aromatic ring, $a(^1H) = 3.17$ G, and $^{107,109}Ag$ (nuclear spin $I = {}^1/_2$ for both isotopes), $a(^{107,109}Ag) = 1.67$ G. Our values of hyperfine interaction constants at high temperatures, as well as the *g*-factor of the complex, $g = 2.0030$, are the same as previously reported.[10] The value $a(^1H) = 3.17$ G for the silver complex is close to the values of $a(^1H) = 3.0-3.3$ G for $SQ^{\bullet-}$ radicals with alkali metals,[10] which shows that the O−Ag chemical bond in the silver complex is essentially ionic. For comparison, we can mention that, for 3,6-di-*tert*-butyl-2-R-oxyphenoxide radicals ($SQ^{\bullet}R$) with covalent chemical bonds O−R, $a(^1H) > 3.90$ G.[12,13,17]

As can be seen from Figure 1, with the temperature lowering, the central component (with total value of nuclear spin projection $\sum m_I(^1H) = 0$) of the triplet due to the two protons experiences faster broadening than the components with $\sum m_I(^1H) = \pm 1$. This can be visualized by noticing the change in the amplitude ratio of the proton triplet components in the EPR spectra (marked with dots in Figure 1) from 1:2:1 at high temperatures to about 1:1:1 at 190 K in toluene (Figure 1). This alternating line width effect is due to dynamic charge and electron spin redistribution within silver atom and two oxygen atoms in the complex:

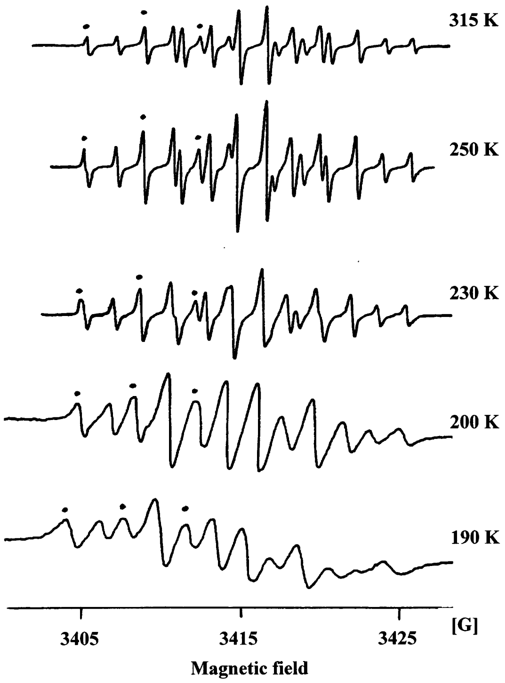
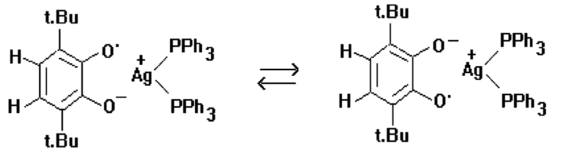


Figure 1. EPR spectra of the $SQ^{\bullet-}Ag^+(PPh_3)_2$ complex in toluene at different temperatures. Low-field components of the triplet hyperfine splitting due to protons in the $SQ^{\bullet-}$ ligand are marked with dots.



(1)

($SQ^{\bullet-}Ag^+(PPh_3)_2$ complex)

At high temperatures, when the above exchange process is fast in the EPR time scale, the two protons in the aromatic ring of the $SQ^{\bullet-}$ ligand are equivalent. In the slow exchange limit, the two protons become nonequivalent, so that the hyperfine interaction constants, $a(^1H)_{meta}$ and $a(^1H)_{para}$, due to ^1H nuclei in the meta and para positions with regard to the monovalent oxygen atom $O^{\bullet}$ are different. There is a simple relationship between the values of proton hyperfine interaction constants in fast and slow exchange limits, i.e., $a(^1H) = [\ a(^1H)_{meta} + a(^1H)_{para}]/2$. According to previous data on absolute values of $a(^1H)_{meta}$ and $a(^1H)_{para}$ for a variety of radicals and complexes with $SQ^{\bullet-}$ ligands, $a(^1H)_{para} > a(^1H)_{meta}$.[17] The difference $\Delta a = a(^1H)_{para} - a(^1H)_{meta}$ for ionic complexes is usually $\Delta a \approx 0.3$ G,[17] which in the present case of the $SQ^{\bullet-}Ag^+(PPh_3)_2$ complex is close to the width of individual lines of the EPR spectrum in the fast exchange limit at high temperatures. This is the reason we were not able to observe actual separation of the central component ($\sum m_I(^1H) = 0$) into two individual lines at low temperatures.

Further analysis of the EPR spectra shows that the values $a(^1H)$ and $a(^{107,109}Ag)$ are temperature independent. The two ^{31}P nuclei from two phosphine ligands in $SQ^{\bullet-}Ag^+(PPh_3)_2$ remain equivalent at all temperatures. The relatively small values

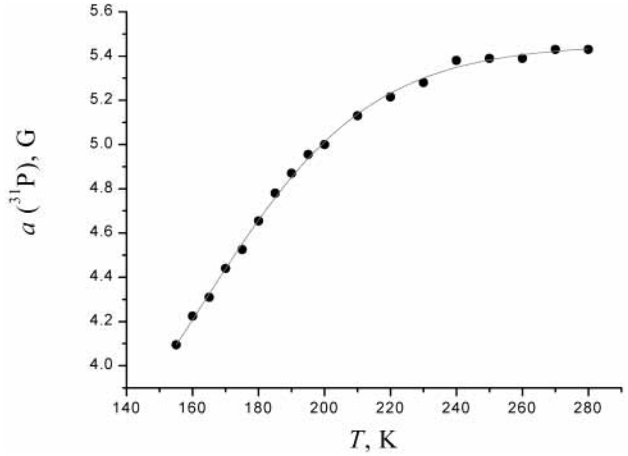


Figure 2. Temperature dependence of the ^{31}P hyperfine interaction constant in the $SQ^{\bullet-}Ag^{+}(PPh_3)_2$ complex in pentane.

of $a(^{31}P) = 4-5.5$ G for the $SQ^{\bullet-}Ag^{+}(PPh_3)_2$ complex, compared to the values of $a(^{31}P) = 16-17$ G for trigonal-pyramidal copper complex $SQ^{\bullet-}Cu^{+}(PPh_3)_2$,[10] suggest that two P atoms of the PPh_3 ligands in the silver complex are located near the π-plane of the radical ligand. This should result in planar structure of the $SQ^{\bullet-}Ag^{+}(PPh_3)_2$ complex. In Figure 2 we present the temperature dependence of $a(^{31}P)$ in pentane, which has a lower freezing point and therefore allows measurements of the $a(^{31}P)$ values in a broader temperature range. It can be seen from Figure 2 that $a(^{31}P)$ increases with the temperature increase. This effect is well known for organic π-radicals and π-radical complexes, where hyperfine interaction of the unpaired electron with atoms in substituted groups is based on hyperconjugation.[18] In the case of this complex, lower values of $a(^{31}P)$ are expected at lower temperatures when two P atoms along with the central Ag atom are on the π-plane of the radical ligand. At higher temperatures, due to intramolecular motions, the planar structure of the complex can be distorted such that two P atoms can move slightly out of the π-plane. This will increase hyperconjugation between π-orbitals of the radical ligand and atomic orbitals of phosphorus, and therefore increase the value of $a(^{31}P)$.

It is interesting to see that $a(^{31}P)$ approaches its maximum value at approximately the same temperatures where we observe a symmetrical charge distribution between two oxygen atoms of the $SQ^{\bullet-}$ ligand. This means that the charge redistribution process (1) within central metal ion and radical ion ligand is actually accompanied by motion of the other two neutral ligands. In other words, dynamic charge redistribution in the complex is the result of motion of the entire coordination sphere.

The characteristic frequency or the rate constant k_{ex} of the exchange process (1) can be estimated from the following well-known equation,[19]

$$k_{ex} = (2/3)^{1/2}\gamma_e(\Delta a)^2/8\delta_{ex} \tag{2}$$

where γ_e is the magnetogyric ratio for the electron and δ_{ex} is the contribution to the line width due to exchange reaction (1). To calculate the values of k_{ex} from eq 2, we used the above-mentioned value of $\Delta a = 0.3$ G and the values of δ_{ex} determined from the experimental EPR spectra at different temperatures. The δ_{ex} values were conveniently determined using the relation

$$2A_1\delta^2 = A_0(\delta + \delta_{ex})^2 \tag{3}$$

where A_0 and A_1 are the amplitudes of the proton hyperfine line components with $\sum m_I = 0$ and $\sum m_I = \pm 1$, respectively, and δ is the line width of the component with $\sum m_I = \pm 1$. Equation 3 reflects the fact that the intensity ratio (not the amplitude ratio) in the triplet splitting due to two aromatic protons of the $SQ^{\bullet-}$ ligand in the fast exchange limit is always 1:2:1. This procedure correctly determines the values of δ_{ex} from easily measurable values of A_0, A_1, and δ. The latter is a pick-to-pick line width of the low-field component of the EPR spectra in Figure 1, and changes due to temperature-dependent changes in solvent viscosity.

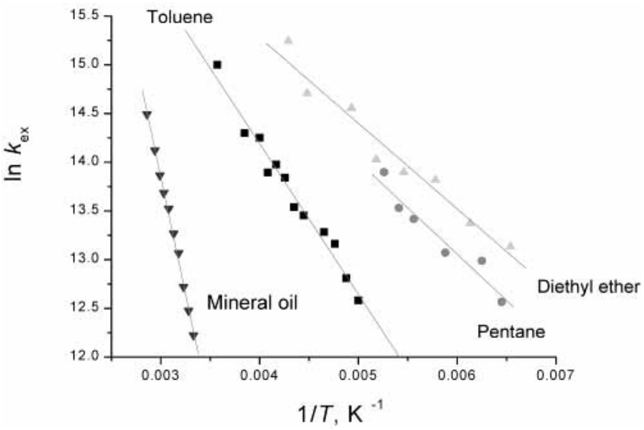


Figure 3. Arrhenius plot for the rate constant k_{ex} of the exchange reaction (1) in different solvents.

TABLE 1: Kinetic Parameters of the Exchange Reaction (1) for the Ag^{+} Complex in Different Solvents, and Kinetic Parameters of the Exchange Transition (5) for the Cu^{+} Complex in Toluene

solvent	k°_{ex}, s^{-1}	E_a, kcal/mol	k_{ex}, s^{-1} at 300 K
diethyl ether	$(1.45 \pm 0.15) \times 10^{8}$	1.8 ± 0.2	$(7.7 \pm 0.8) \times 10^{6}$
pentane	$(1.4 \pm 0.2) \times 10^{8}$	1.9 ± 0.3	$(5.9 \pm 0.6) \times 10^{6}$
toluene	$(7.1 \pm 0.7) \times 10^{8}$	3.1 ± 0.2	$(4.1 \pm 0.4) \times 10^{6}$
(Cu^{+} complex)	$(4.9 \pm 0.5) \times 10^{12}$	5.1 ± 0.2	$(9.6 \pm 0.9) \times 10^{8}$
mineral oil	$(1.8 \pm 0.2) \times 10^{12}$	9.6 ± 0.2	$(0.21 \pm 0.02) \times 10^{6}$

In Figure 3 we present the temperature dependence of the rate constants k_{ex} in different solvents. The temperature dependence of k_{ex} can be described by the Arrhenius relation,

$$k_{ex} = k^{\circ}_{ex}\exp(-E_a/RT) \tag{4}$$

The values of the pre-exponential factor k°_{ex} and activation energy E_a are presented in Table 1. In high-viscosity solvents such as mineral oil, the rate of the intramolecular charge-transfer reaction (1) decreases by about 30 times compared to that in nonviscous solvents. This confirms the involvement of bulky ligands' motion in the charge redistribution dynamics of the $SQ^{\bullet-}Ag^{+}(PPh_3)_2$ complex.

It is interesting to compare some structural and dynamic features of $SQ^{\bullet-}Ag^{+}(PPh_3)_2$ and the related copper complex, $SQ^{\bullet-}Cu^{+}(PPh_3)_2$. EPR spectra of the copper complex reveal an interaction of the unpaired electron with two equivalent protons of the $SQ^{\bullet-}$ ligand, $a(^{1}H) = 3.0$ G, two equivalent phosphorus atoms at high temperatures, $a(^{31}P) = 16.0$ G, and ^{63}Cu and ^{65}Cu nuclear isotopes ($I = {}^{3}/_{2}$ for both isotopes), $a(^{63}Cu) = 11.0$ G and $a(^{65}Cu) = 12.0$ G. As can be seen from the EPR spectra of the copper complex in Figure 4, the two aromatic protons in the $SQ^{\bullet-}$ ligand in the complex remain equivalent at all temperatures. This shows a symmetric distribution of the charge within two oxygen atoms of the radical anion ligand and the Cu^{+} cation on the EPR time scale, which is on the order of $10^{-10}-10^{-9}$ s. (It would be interesting to see if this charge-

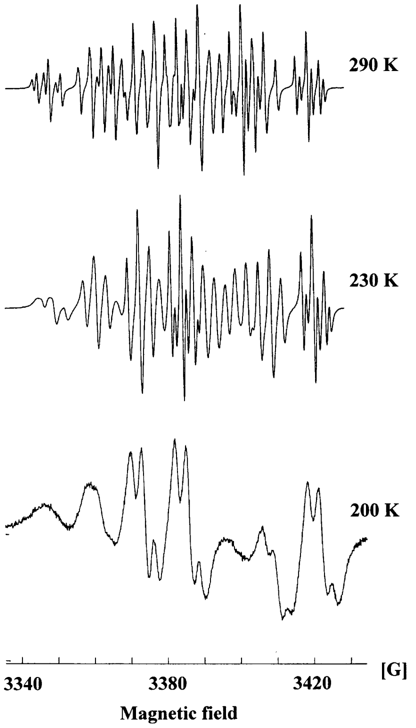
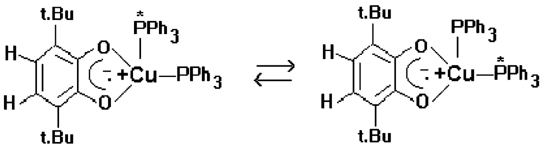


Figure 4. EPR spectra of the $SQ^{\bullet-}Cu^{+}(PPh_3)_2$ complex in toluene at different temperatures.

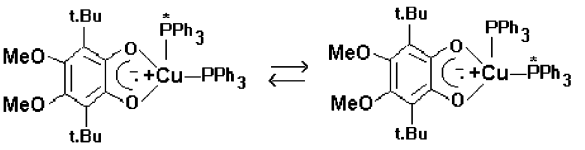
symmetry is maintained on the time scale of vibrational relaxation, i.e., 10^{-13}–10^{-11} s. For this research purpose, the Raman scattering technique can be applied.[11]) On the other hand, for this copper complex we observe alternating line width effect for hyperfine splitting due to two the ^{31}P nuclei of the PPh_3 ligands. They are magnetically equivalent and demonstrate nearly a 1:2:1 amplitude ratio for the phosphorus triplet splitting in the EPR spectrum at $T > 330$ K. At lower temperatures, the central line of the triplet with $\sum m_I(^{31}P) = 0$ broadens and vanishes in the transition to the slow exchange limit between the positions of PPh_3 ligands in the complex:



(5)

($SQ^{\bullet-}Cu^{+}(PPh_3)_2$ complex)

The kinetics of the intramolecular transition (5) and the reorientation dynamics of the similar copper complex $(MeO)_2$-$SQ^{\bullet-}Cu^{+}(PPh_3)_2$ with two MeO radicals in the 4,5-positions of the $SQ^{\bullet-}$ ligand were studied in our previous work:[16]



(5')

($(MeO)_2SQ^{\bullet-}Cu^{+}(PPh_3)_2$ complex)

The simplest possible ligand rearrangement to realize the above processes is that the equatorial PPh_3 ligand goes down and becomes axial, so that the other PPh_3 ligand goes from up-down to the equatorial position. Such a mechanism will lead to the exchange processes (5) and (5′). The EPR spectrum parameters for these two copper complexes are very close to each other, except that for the complex $SQ^{\bullet-}Cu^{+}(PPh_3)_2$ there is additional triplet splitting of each line due to the protons in the 4,5-positions of the aromatic ring. The structure of the $(MeO)_2SQ^{\bullet-}Cu^{+}(PPh_3)_2$ complex was studied in detail on the basis of both isotropic and anisotropic EPR spectrum parameters.[16] This complex has trigonal pyramidal structure with two different positions of the PPh_3 ligands with respect to the π-plane of the paramagnetic ligand, equatorial and axial. In the fast exchange regime, the value of $a(^{31}P)$ in the phosphorus triplet is $a(^{31}P) = [a(^{31}P)_{axial} + a(^{31}P)_{equatorial}]/2$. For the complex $(MeO)_2SQ^{\bullet-}Cu^{+}(PPh_3)_2$, $a(^{31}P) = 15.0$ G, $a(^{31}P)_{axial} = 21.0$ G, and $a(^{31}P)_{equatorial} = 9.0$ G.[16] Isotropic values $a(^{31}P)_{axial}$ and $a(^{31}P)_{equatorial}$ for the complex $SQ^{\bullet-}Cu^{+}(PPh_3)_2$ cannot be found from liquid solution EPR spectra, because the actual split of the central line of the phosphorus triplet into two lines may occur at temperatures below the freezing point of the solution. As it was previously shown for the complex $(MeO)_2SQ^{\bullet-}Cu^{+}(PPh_3)_2$,[16] the anisotropy of the ^{31}P hyperfine interaction in both axial and equatorial positions is about 3 G. For the complex $SQ^{\bullet-}Cu^{+}(PPh_3)_2$, this is the value of the hyperfine interaction constant due to the protons in the $SQ^{\bullet-}$ ligand. Therefore, when we consider the anisotropic EPR spectrum of the complex $SQ^{\bullet-}Cu^{+}(PPh_3)_2$ (see Figure 5a), to a good approximation we can assume that the hyperfine interaction constants due to both the axial and equatorial phosphorus atoms in $SQ^{\bullet-}Cu^{+}(PPh_3)_2$ are isotropic. In this case, the value of $a(^{31}P)_{axial}$ can be easily measured from the anisotropic EPR spectrum of the complex $SQ^{\bullet-}Cu^{+}(PPh_3)_2$, as shown in Figure 5a. From this measurement, we find that $a(^{31}P)_{axial} = 21.5$ G, which is very close to $a(^{31}P)_{axial}$ for the $(MeO)_2SQ^{\bullet-}Cu^{+}(PPh_3)_2$ complex and makes our approximation credible. Now, from the values of $a(^{31}P)$ and $a(^{31}P)_{axial}$ for $SQ^{\bullet-}Cu^{+}(PPh_3)_2$, we find that, for this complex, $a(^{31}P)_{equatorial} = 10.5$ G. This value for the Cu complex is remarkably larger than the value of $a(^{31}P) = 4.1$ G for the Ag complex at low temperatures, when the phosphorus atom is also near the π-plane of the radical ligand in the Ag complex. Such a difference in the ^{31}P hyperfine splittings could be due to the difference in the values of the electron spin density on Ag and Cu atoms. However, the experimental ratio of $a(^{63,65}Cu):a(^{107,109}Ag) \approx 6.8$ is close to the average magnetic momentum ratio $\mu(^{63,65}Cu)$: $\mu(^{107,109}Ag) \approx 6.3$. This means that the electron spin densities

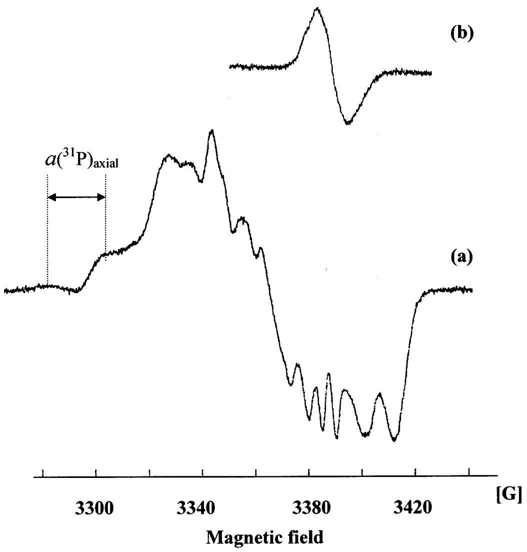


Figure 5. EPR spectra of the $SQ^{\bullet-}Cu^{+}(PPh_3)_2$ (a) and $SQ^{\bullet-}Ag^{+}(PPh_3)_2$ (b) complexes in frozen toluene solution at 77 K.

on the central ions are approximately the same for Ag and Cu complexes. Therefore, the difference in the values of $a(^{31}P)$ in Ag and Cu is related to the difference in the efficiency of overlapping of the 4d and 3d orbitals with the atomic orbitals of phosphorus.

According to the reaction shown in eq 1, one can also consider a possible three-coordinate structure for the Ag complex, with one oxygen atom of the $SQ^{\bullet-}$ ligand forming an ionic bond and the two phosphorus atoms of the phosphine ligands forming coordination bonds. However, one needs to keep in mind that the second oxygen atom should not be completely free of any kind of coordination to the Ag^+ ion. Otherwise, it would be unlikely to see any two-oxygen-atom coordination dynamics of the complex that we observed. Therefore, we consider a distorted tetracoordinated Ag(I) complex, in which one oxygen atom forms an ionic bond with the metal and the other forms a weak coordination bond with the metal. From this point of view, the complex can be treated as three-coordinate, meaning that it has three relatively strongly attached atoms (O, P, P) in its coordination sphere and one weakly bonded O atom. If we compare relative tendencies for three- vs four-coordination between Ag and Cu, we can see that the four-coordinate structure of the Cu complex is more pronounced.

In Figure 5a,b we compare frozen solution EPR spectra of copper and silver complexes, $SQ^{\bullet-}Cu^+(PPh_3)_2$ and $SQ^{\bullet-}Ag^+(PPh_3)_2$. One can see that, in contrast to that of the copper complex, the EPR spectrum of the silver complex is essentially isotropic. Since we already found that hyperfine interaction due to phosphorus is isotropic, the magnetic anisotropy of the copper complex should arise from anisotropy of both the *g*-factor and hyperfine interaction of the unpaired electron with copper. This conclusion can also be made from the liquid solution EPR spectra of the $SQ^{\bullet-}Cu^+(PPh_3)_2$ complex (Figure 4). Indeed, the components of the quartet of lines due to $^{63,65}Cu$ hyperfine splitting have different line widths, which directly shows the anisotropy of both the *g*-factor of the complex and the $^{63,65}Cu$ hyperfine interaction constant. However, it is rather difficult to correctly obtain anisotropic *g*-factor values and $^{63,65}Cu$ hyperfine interaction constants from the EPR spectrum in Figure 5a. In our previous work, this problem was solved for the complex $(MeO)_2SQ^{\bullet-}Cu^+(PPh_3)_2$ by employing very high-frequency EPR (140 GHz) and obtaining the **g**-tensor values, $g_{xx} = 2.0078$, $g_{yy} = 2.0059$, $g_{zz} = 1.9991$.[16] Although no hyperfine splitting was resolved at 140 GHz, the anisotropic values of the $^{63,65}Cu$ hyperfine interaction ($A_{xx} = 20.0$ G, $A_{yy} = 0.0$ G, $A_{zz} = 17.0$ G) were found using the correct **g**-tensor values with further computer simulations of the frozen solution EPR spectrum at 9.6 GHz.[16]

Having obtained the values $a(^{31}P)_{\text{axial}}$ and $a(^{31}P)_{\text{equatorial}}$ for the complex $SQ^{\bullet-}Cu^+(PPh_3)_2$, we can now determine the rate constants k_{ex} of the exchange process (5) at different temperatures. The values of k_{ex} can be calculated from eq 2, where $\Delta a = a(^{31}P)_{\text{axial}} - a(^{31}P)_{\text{equatorial}} = 11.0$ G. In Figure 6 we present the temperature dependence of k_{ex} for reaction 5. It is described by the Arrhenius equation (4), with the values of k°_{ex} and E_a given for comparison in Table 1, along with the kinetic parameters of the reaction 1 for silver complex in toluene. As we can see, the dynamics of the coordination sphere due to neutral ligands' rearrangement in the complex $SQ^{\bullet-}Cu^+(PPh_3)_2$ is about 2 orders of magnitude faster than the dynamics of charge redistribution within the radical anion ligand and the central metal cation in the $SQ^{\bullet-}Ag^+(PPh_3)_2$ complex. In ref 16, we showed that the dynamics of neutral ligand rearrangement (5′) is linearly correlated with solvent reorientation dynamics and the two processes occur with comparable frequencies, as can be expected for exchange of bulky ligands such as PPh_3.

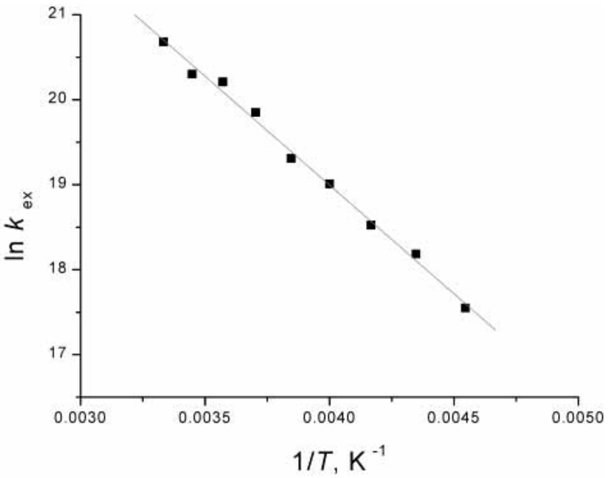


Figure 6. Arrhenius plot for the rate constant k_{ex} of the intramolecular exchange transition (5) in toluene.

What is less obvious is that the rate of charge redistribution of the innermost space of the complex is also controlled by the dynamics of the nonpolar solvent, as we have shown for the case of reaction 1 for the silver complex in mineral oil. This finding is consistent with the present knowledge on the strong influence of solvent reorganization energy λ_S on the kinetics of condensed-phase electron transfer.[20,21] In polar solvents, the primary contribution to λ_S arises from modulation of the dipole−dipole interaction between solvent and reactant molecules by solvent reorientation.[22−24] In nonpolar solvents, the polar reactant molecule induces dipole moments in solvent molecules, so that solvent molecular mobility can again modulate electron-transfer rates.[21,25−27] If we compare the rates of the processes (1) and (5) in toluene (Table 1), the rate constant ratio $k_{ex,(5)}/k_{ex,(1)} \approx 10^2$ roughly represents the average number of molecular rearrangements per one elementary act of the intramolecular electron transfer (1).

Conclusions

EPR spectroscopic analyses of Ag^+ and Cu^+ complexes with a substituted *o*-semiquinone radical anion ligand and two neutral PPh_3 ligands reveal the structure and intramolecular dynamics of these complexes. In both complexes, the oxygen−metal chemical bond is ionic. In the silver complex, asymmetric charge distribution within two oxygen atoms of the radical anion and Ag^+ has been observed along with the dynamic electron exchange between two oxygen atoms. Two PPh_3 ligands in the silver complex tend to move within the coordination sphere of the complex but take symmetric positions with regard to the π-plane of the radical anion ligand and the silver atom. In the copper complex, we have found temperature-independent symmetric charge distribution within two oxygen atoms of the radical anion and Cu^+, but different positions of the two PPh_3 ligands. The complex has a trigonal pyramidal structure, with one phosphorus atom in an axial position and the other in an equatorial position with regard to the π-plane of the radical anion ligand and copper atom. We have observed dynamic reorganization in the coordination sphere of the copper complex, which is the exchange in the positions of PPh_3 ligands in the complex. The rate of this process is on the order of solvent reorientation frequencies, while the intramolecular electron exchange rates in the Ag^+ complex are about 2 orders of magnitude lower. By going from a nonpolar, nonviscous solvent, pentane, to a nonpolar, viscous solvent, mineral oil, the electron exchange rate constant further decreases by about 30 times. This shows that the electron exchange in the Ag^+ complex is controlled by nonpolar solvent dynamics.

Acknowledgment. Financial support for this work was provided by NASA, HBCU Group 3 University Research Centers (URC) program at Norfolk State University, the King Fahd University of Petroleum and Minerals, and the Russian Foundation for Fundamental Research under Grant 02-03-33060. T.N.H. gratefully acknowledges support for the undergraduate research assistantship provided by the Center for Materials Research at Norfolk State University.

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