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# An ESR Study of the Reaction of Copper Clusters $Cu_3$ and $Cu_5$ with Molecular Oxygen at 77 K in a Rotating Cryostat[1]

The interaction of molecules with small metal clusters can provide insight into the nature of the adsorbed species on catalytic metal surfaces and may provide information about the mechanisms of heterogeneous reactions (*1–5*). Dioxygen is one of the simplest adsorbates and has been extensively studied on metal surfaces because of its involvement in technically important reactions such as the epoxidation of ethylene and the oxidation of alcohols (*6*) and alkenes (*7*). Despite use of conventional techniques and modern methods of surface physics controversy still remains about the nature of the active oxygen moiety (*8–12*). We have recently described the use of a rotating cryostat to prepare naked metal clusters of silver (*13*), copper (*14*), and gold (*15*) and to show that silver and gold atoms react with oxygen at 77 K to form symmetrically bridged species with $C_{2v}$ symmetry while copper atoms form a conventional peroxyl of $C_s$ symmetry (*16*). Ozin *et al.* (*17*) have concluded from uv–visible absorption/fluorescence and infrared spectroscopic studies that copper atoms, photoexcited to the $^2P$ state, react with molecular oxygen to give OCuO while the ground state atoms give a tight ion pair with nonequivalent oxygen atoms. Here we report on the reaction of molecular oxygen at 77 K with $Cu_3$ and $Cu_5$ clusters, produced by photoexcitation of copper atoms on the surface of frozen adamantane and cyclohexane, respectively, to give $Cu_3^+O_2^-$ and $Cu_5^+O_2^-$.

The experimental technique used to deposit copper atoms from a small high-temperature furnace onto a continually renewed frozen matrix layer deposited from a previous jet on the surface of a rotating drum at 77 K has been described (*18*). For the present experiments light from a 250-W extra-high-pressure mercury lamp was focused on the surface layer between the copper furnace and oxygen jet. Deposits were removed from the drum at 77 K and transferred to a tube suitable for ESR investigation. ESR spectra were recorded on a Varian E-4 spectrometer. The microwave frequency was measured with a Systron–Donner Model 6016 frequency counter and the magnetic field with a Varian E-500 NMR gaussmeter. $^{63}CuO$ was obtained from Oak Ridge National Laboratory, Tennessee, and was reduced to $^{63}Cu$ (98.89%) with hydrogen at 500°C. Adamantane and cyclohexane were obtained from Aldrich.

The ESR spectrum given by photolyzed $^{63}Cu$ atoms and molecular oxygen trapped in adamantane is shown in Fig. 1a. The spectrum is dominated by the signal from three quartets centered at $g = 2.081$, 2.007, and 2.000 which are assigned to the copper peroxyl $CuOO^\cdot$ (*16*). In addition to this spectrum there is a less-intense multilined feature centered at $g = 2.261$ with a line spacing of 28 G. This feature is shown in expanded scale and at higher gain in Fig. 1b. It is best analyzed in terms of 10 lines with intensity ratios 1:3:6:10:12:12:10:6:3:1 and is assigned to a species with three equivalent $^{63}Cu$ atoms. The magnitude of the *g*-factor and the shape of the spectrum suggest that it is the parallel feature of an anisotropic spectrum with the perpendicular features masked by the spectrum from $CuOO^\cdot$. This spectrum is tentatively assigned to a $^{63}Cu_3$–

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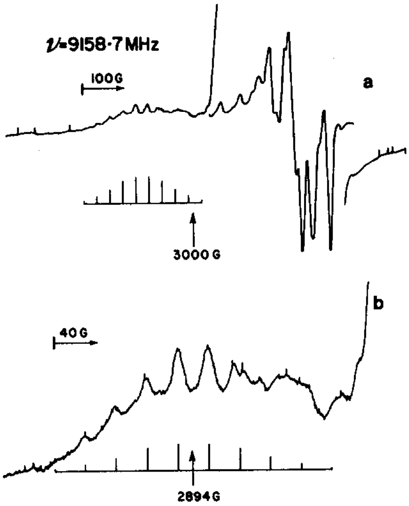

FIG. 1. ESR spectrum of the products from the reaction of photolyzed Cu atoms with $O_2$ trapped in adamantane at 77 K. (a) Full spectrum dominated by $CuOO^·$ and (b) the 10-line feature assigned as a parallel feature of $Cu_3^+O_2^-$.

$O_2$ complex because in the absence of $O_2$ the trimer, $^{63}Cu_3$, with two equivalent and one unique Cu atom, is the major paramagnetic cluster produced by photolyzed $^{63}Cu$ atoms in adamantane (*14*).

When cyclohexane is used as the inert matrix the spectrum shown in Fig. 2a is obtained. This spectrum is again dominated by the anisotropic spectrum from $CuOO^·$. There are, however, extra lines in the center of the spectrum and a wider and more complex parallel feature centered at $g = 2.26$, which contains more lines than the analogous feature from $Cu_3$–$O_2$. The spectrum shown in Fig. 2b shows the parallel region at higher gain and in expanded scale after the sample had been annealed at 118 K. The spectrum at this temperature is less complex than at 77 K partly because parallel features from $Cu_3$–$O_2$ and a possible second site for the multilined spectrum disappear. There do, however, appear to be 8 lines at fields below the center of the spectrum suggesting a 16-line spectrum which is consistent with a $Cu_5$ species with 5 equivalent copper nuclei. Since $Cu_5$ is formed in the absence of $O_2$ and the ESR spectrum shown in Fig. 2 is only formed in the presence of $O_2$ we tentatively suggest that the species responsible for the spectrum is the copper–oxygen complex $Cu_5$–$O_2$. The separations of the lines suggest a value of $A_{\parallel}$ (Cu) ~ 25 G.

In some additional experiments $O_2$ was introduced into the cryostat after $Cu_3$ and $Cu_5$ had been prepared in adamantane and cyclohexane, respectively, at 77 K. In both cases the surface coloration of the deposit was observed to change during this operation. The ESR spectrum of the reaction products in adamantane showed very strong spectra from $Cu_3$ and $CuOO^·$ and the weak parallel features shown in Fig. 1b. Similarly the reaction products in $c$-$C_6H_{12}$ gave an intense spectrum from $Cu_5$, a weak signal from CuOO. with extra central lines and the parallel features shown in Fig. 2b. It is apparent from these experiments that although $O_2$ does not diffuse into the main body of the matrix sufficient is absorbed to react with surface clusters, $Cu_3$ in adamantane and $Cu_5$ in $c$-$C_6H_{12}$, to give $Cu_3$–$O_2$ and $Cu_5$–$O_2$. Unfortunately, the perpendicular

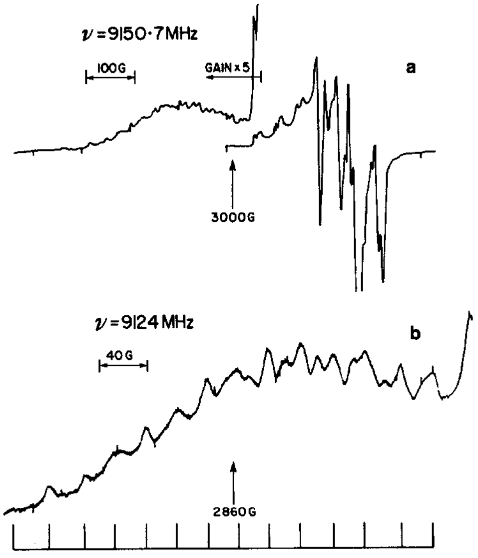

FIG. 2. ESR spectrum of the products from the reaction of photolyzed Cu atoms with $O_2$ trapped in cyclohexane at 77 K. (a) Full spectrum dominated by $CuOO^·$ and (b) the low-field feature assigned as a parallel feature of $Cu_5^+O_2^-$.

($g_{xx}$ and $g_{yy}$, if the species are not axially symmetric) features in the $g \sim 2$ region are not be obtained sufficiently free from CuOO, by varying the deposition conditions or annealing the samples, and complete spectral analysis is not possible. Furthermore, the spectra are too weak and complex to contemplate $^{17}O$ labeling experiments to confirm the number of oxygen atoms associated with each cluster. Despite these limitations the observation of $Cu_5$ *and* $Cu_5$–$O_2$ and $Cu_3$ *and* $Cu_3$–$O_2$ in the same samples constitutes good evidence for the assignment of the dioxygen species to cluster reactions with oxygen. We also tentatively conclude from variations in the oxygen and cluster concentrations that each cluster interacts with one oxygen molecule.

Although the structure of the oxygenated clusters cannot be established unambiguously the high $g$ values and the near equivalence of the low Cu 4$s$ spin populations for these two species (~0.04 for $Cu_3$–$O_2$ and ~0.06 for $Cu_5$–$O_2$, assuming similar contributions in the parallel and perpendicular directions) indicates that they are not peroxyls of the type $Cu_nO\dot{O}$ but that electron transfer has occurred from the neutral clusters to molecular oxygen to give $O_2^-$ and $Cu_n^+$ which are held together largely by electrostatic attraction. $Cu_3$ and $Cu_5$, therefore, behave like the alkali metal atoms ($M$) which react with oxygen to give $M^+O_2^-$ (*19,20*). Further support for this identification comes from the measured ionization potentials of Cu clusters in supersonic beams which puts the ionization potentials for $Cu_3$ and $Cu_5$ between 4.98 and 6.4 eV (*21, 22*). This range is considerably lower than the I.P. for $Cu^{23}$ (7.726 eV) which does not undergo charge transfer with oxygen but is similar to the value for $Na^{23}$ (5.139 eV) which does.

Unlikely alternatives are the oxides $Cu_nO^+$ and $Cu_nO$. The former have been produced by reaction of small metal clusters with oxygen in continuous beams of refractory metals ionized with an excimer laser-pumped dye laser (*24*) and can be discounted because they are not paramagnetic unless they occur in a high spin state. We are disinclined to suggest $Cu_3O$ and $Cu_5O$ with structures analogous to CuOCu (*25*) because dissociation of the cluster and oxygen is unlikely to occur under the mild conditions of the present experiments.

The free electron in $Cu_3^+O_2^-$ and $Cu_5^+O_2^-$ must reside mainly (~95%) in the $1\pi_g^*$ antibonding orbital of $O_2^-$ with a small residual spin population on the ionized copper cluster as found in the alkali metal superoxides (*19, 20*). The large positive $g_\parallel$ shift of ~0.25 is similar to that found in these superoxides and results from the very small energy separation between the two nearly degenerate $\pi_g^*$ orbitals. An additional factor in the $Cu_n^+O_2^-$ clusters will be the small contribution of copper $d$-orbitals to the SOMO which will also raise the value of $g_\parallel$. The $g_\parallel$ shift is larger than the $g_\parallel$ shift found for the $O_2^-$ species on metallic silver deposited in Vycor glass ($\Delta g_\parallel \sim 0.034$) (*26*). The latter give shifts close to the value for $O_2^-$on metal oxides (*11*) which has been taken to indicate that the oxygen is adsorbed on an oxidized surface and not a virgin silver surface. The $O_2^-$ species observed in the present work is likely to be that resulting from direct reaction with the "surface" of the metal clusters. We are not aware of any ESR studies of the adsorption of oxygen on copper surfaces but the reduction in vibrational frequencies from EELS studies for $O_2$ adsorbed on silver and copper surfaces at low temperatures is attributed to electron transfer from the metal to the $1\pi_g^*$ antibonding orbital of $O_2$ and back-donation from the $1\pi_u$ bonding orbital to the metal (*27, 28*). The present results are consistent with this. Furthermore theoretical calculations (*29*) predict that $Cu_3^+$ and $Cu_5^+$ will have equilateral triangular and trigonal bipyramidal geometries, respectively, with all the copper centers equivalent. In the context of catalysis it is worth noting that the electron-transfer process results in a change in geometry of the copper clusters from nearly linear to triangular for $Cu_3$ and a distorted to a regular trigonal bipyramidal for $Cu_5$, i.e., the metal ensemble is mobile.

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