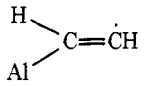
Copper Atom–Acetylene Complexes. Matrix Isolation Electron Spin Resonance Study

Sir:

Metal atom chemistry, the study of reactions of metal atoms with organic and inorganic molecules, has been the subject of many investigations.[1] Recently, we have shown that Al atoms and acetylene molecules cocondensed in rare-gas matrices react to form the addition product having the vinyl structure i.[2]



i

We report, in this communication, the electron spin resonance (ESR) study of copper atom–acetylene molecular complexes generated in rare-gas matrices. The spectral analysis revealed the formations of mono- and diacetylene complexes, $Cu(C_2H_2)$ and $Cu(C_2H_2)_2$. It is concluded that both complexes are stabilized by the dative bonds resulting from the interaction between the π orbitals of acetylene and the valence orbitals (3d, 4s, and 4p) of the Cu atom.

The experimental setup designed to trap high temperature vapor phase species in a rare-gas matrix at liquid helium temperature and to observe the ESR of the resulting matrix was described earlier.[3] In the present series of experiments, Cu atoms were vaporized from a resistively heated tantalum cell and trapped in argon matrices containing acetylene. The concentration of acetylene was varied from 0.3 to 10 mol %, and that of Cu was maintained at ~0.1 mol %. The spectrometer frequency locked to the sample cavity was 9.41 GHz.

The ESR spectrum observed from an argon matrix containing Cu and C_2H_2 (2%) is shown in Figure 1. Three different types of signals, A, B, and C, are indicated. The signals A are due to isolated Cu atoms ($3d^{10}4s^1$). Owing to the large hyperfine interaction with ^{63}Cu (natural abundance = 69%, $I = 3/2$, $\mu = 2.2206\ \beta_N$) and ^{65}Cu (natural abundance = 31%, $I = 3/2$, $\mu = 2.3790\ \beta_N$), only two transitions of Cu atoms are observable; one transition corresponding to the "NMR" transition $M_S = -1/2$, $M_I = -1/2 \rightarrow -3/2$ occurs at 1.5 and 2.0 KG for ^{63}Cu and ^{65}Cu, respectively, and the other corresponding to the ESR transition $M_S = -1/2 \rightarrow +1/2$, $M_I = -3/2$ occurs at 5.8 and 6.0 KG.[4] The signals B and C are unique to the matrices containing Cu and acetylene. As indicated in the figure the signals B were recognized as two sets of quartets arising from the hyperfine interactions with ^{63}Cu and ^{65}Cu nuclei, respectively. The spectrum C consists of many hyperfine components placed symmetrically within a narrow range (±200 G) of the position corresponding to $g = 2.00$. It is shown in Figure 2a in an expanded scale. When the matrix was prepared using less acetylene (0.3 mol %), the Cu atom signals A became stronger and the B signals appeared essentially unchanged, while the C signals became barely observable. When the acetylene concentration was increased to 10 mol %, the C signals became extremely intense, but the A and B signals were no longer observed. It is thus strongly suggested that a greater number of acetylene molecules are involved in complex C than in B. Figure 2b shows the spectrum C observed when the matrix was prepared using perdeuterioacetylene (C_2D_2, 2 mol %). No discernible effect of the isotopic substitution was noted for the B signals. The quartet pattern resolved in Figure 2b is also attributed to the hyperfine structure due to the Cu nuclei; the difference between the coupling tensors of ^{63}Cu and ^{65}Cu is too small to be resolved and the broader line width of the outer components is caused by the anisotropy of the coupling tensors. A careful examination of Figures 2a and 2b shows that the spectral pattern of Figure 2a is an overlapping quartet of quintets, the quartet spacing being equal to that seen in Figure 2b and the quintet feature being that expected from the hyperfine interaction with four *equivalent* protons. It is proposed, therefore, that the spectrum B be assigned to the monoacetylene complex $Cu(C_2H_2)$ and the spectrum C to the diacetylene complex $Cu(C_2H_2)_2$.

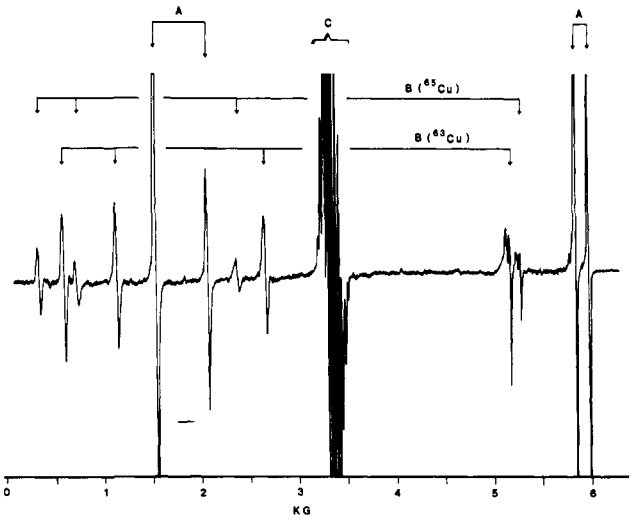


Figure 1. ESR spectrum of an argon matrix containing Cu and acetylene (2 mol %).

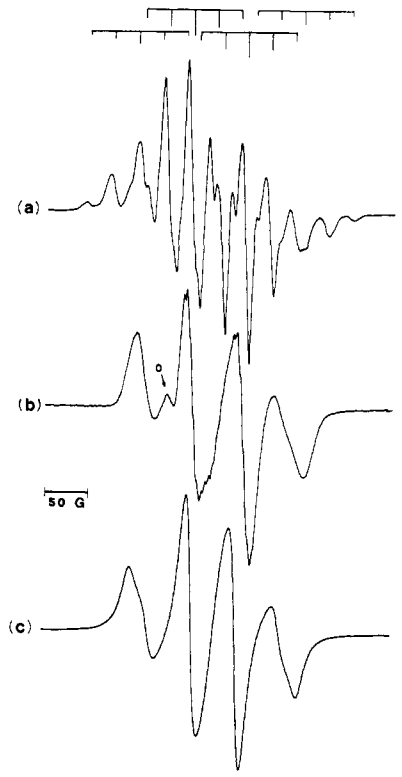


Figure 2. (a) The C signal (of Figure 1) shown in expanded scale. (b) the C signal observed when perdeuterioacetylene (2 mol %) was used. (c) The computer simulated spectrum of the deuterated complex based upon the parameters given in the text.

The line shape of the highest field components of the B spectrum indicates a system having an axially symmetric spin Hamiltonian:

$$H_{spin} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \quad (1)$$

From the observed resonance positions, resorting to the exact diagonalization of the Hamiltonian 1,[4] the following parameters were determined for the monoacetylene complex B:

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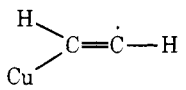
$$g_{\parallel} = 2.008 \pm 0.003$$
$$g_{\perp} = 1.981 \pm 0.003$$
$$A_{\parallel}(^{63}\mathrm{Cu}) = 4098 \pm 7 \text{ MHz}$$
$$A_{\perp}(^{63}\mathrm{Cu}) = 4054 \pm 7 \text{ MHz}$$

As for the diacetylene complex C, resorting to the method of computer simulation (of the ESR spectrum of randomly oriented radicals),[5] the following g and hyperfine coupling tensors were determined from Figures 2a and 2b:

$$g_{\parallel} = g_{\perp} = 2.000 \pm 0.001$$
$$A_{\parallel}(^{63}\mathrm{Cu}) \simeq 0 \text{ G}$$
$$A_{\perp}(^{63}\mathrm{Cu}) = 68 \pm 5 \text{ G}(190 \pm 14 \text{ MHz})$$
$$A_{\parallel}(\mathrm{H}) = A_{\perp}(\mathrm{H}) = 28 \pm 3 \text{ G}$$

The computer-simulated spectrum of $Cu(C_2D_2)_2$ based upon these parameters is shown in Figure 2c. The signal D, indicated by an arrow in Figure 2b, is believed to be caused by an impurity in the C_2D_2 source. Though its intensity increased with increasing C_2D_2 concentration, no signal corresponding to it was observed in the spectra obtained using normal acetylene.

The magnitude of the coupling constant to the Cu nucleus in complex B is ~⅔ of that of isolated Cu atoms. The conspicuous absence of the observable interaction with the protons, however, rules out the vinyl structure ii for this complex. We



ii

suggest the alternative bonding scheme shown in Scheme I. It involves an sp_y hybridization of the Cu atom. The complex is stabilized by the two dative bonds, one resulting from donation of electrons from the bonding π_y orbital into the $sp_y{}^n$ of Cu, and the other resulting from the back-donation from the Cu d_{xy} orbital into the antibonding $\pi_y{}^*$ orbital. The unpaired electron resides in the nonbonding $sp_y{}^{1/n}$ orbital pointing away from the acetylene moiety. The large, essentially isotropic coupling constant to the Cu nucleus and the unobservably small interactions with the protons are thus accounted for.

As for the diacetylene complex C, recalling the presence of four equivalent protons, we suggest the bonding scheme depicted in Scheme II. The Cu atom is flanked by two acetylene molecules arranged symmetrically within the xy plane. The Cu 4s unpaired electron is promoted into the $4p_x$ orbital, and four molecular orbitals are formed that would give rise to the dative interactions within the xy plane

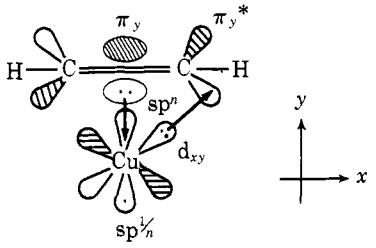
$$a_1\phi_{\mathrm{Cu}}(4\mathrm{s}) + b_1/\sqrt{2}(\pi_y - \pi_y')$$
$$a_2\phi_{\mathrm{Cu}}(4\mathrm{p}_y) + b_2/\sqrt{2}(\pi_y + \pi_y')$$
$$a_3\phi_{\mathrm{Cu}}(3\mathrm{d}_{xy}) + b_3/\sqrt{2}(\pi_y{}^* + \pi_y'^*)$$
$$a_4\phi_{\mathrm{Cu}}(4\mathrm{p}_x) + b_4/\sqrt{2}(\pi_y{}^* - \pi_y'^*)$$

where π_y and π_y' represent the bonding π_y orbitals of the first and second acetylene, respectively. The first two MOs represent the donation of electrons from the bonding π_y orbitals into the Cu 4s and $4p_y$ orbitals, respectively, and the last two MOs represent the back-donation from the filled $3d_{xy}$ and *semifilled* $4p_x$ orbitals into the antibonding $\pi_y{}^*$ orbitals. The Cu coupling tensor of complex C having a small isotropic term and a large anisotropy is explained by the essentially p_x nature of the semifilled orbital. The large, isotropic interaction with the protons is attributed to the direct overlap possible between the $4p_x$ of Cu and the 1s orbitals of the protons. Two other ligand arrangements would also have four equivalent protons: (a) the Cu atom is flanked by two acetylene molecules oriented perpendicular to each other, one in the xy plane as depicted above and the other in the yz plane, and (b) the Cu atom is sided by two acetylene molecules oriented parallel to each other, one in the xy plane as depicted above and the other in the xz plane. The former is ruled out since it does not remove the degeneracy between the Cu p_x and p_z orbitals. A well-defined ESR spectrum with $g \simeq 2.00$ is expected only from a paramagnetic species having a nondegenerate orbital ground state. The second scheme was also deemed unlikely because of the proximity of the filled π orbitals of the acetylene molecules.

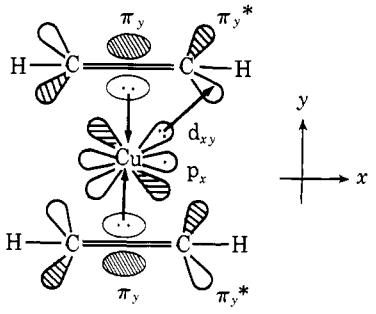
The distribution of the unpaired electron in the vicinity of the Cu nucleus is axially symmetric in both the bonding schemes proposed for the complexes B and C. The Cu coupling tensor is then expected to take the form of $A_{\parallel} = A_{\mathrm{iso}} + 2A_{\mathrm{dip}}$ and $A_{\perp} = A_{\mathrm{iso}} - A_{\mathrm{dip}}$ where A_{iso} represents the interaction arising from the spin density in the 4s orbital, and A_{dip} represents the anisotropic interaction related to the spin density in the 4p orbital.[6] The observed Cu coupling tensors are indeed axially symmetric in both cases. The analyses of the observed tensors gave, for complex B, $A_{\mathrm{iso}} = 4069$ MHz, $A_{\mathrm{dip}} = 15$ MHz; and, for complex C, $A_{\mathrm{iso}} = -127$ MHz, $A_{\mathrm{dip}} = 63$ MHz. The isotropic coupling constant determined for the ^{63}Cu ($3d^{10}4s^1$) atom is 6151 MHz.[4] From the fine structure splitting of Cu atoms in the $3d^{10}4p^1$ state the magnitude of A_{dip} for a 4p electron can be estimated,[7] the result being 68 MHz. We may thus conclude that in complex B the spin densities in the Cu 4s and $4p_y$ orbitals are ~66 and ~22%, respectively, and in complex C the spin densities in the 4s and $4p_x$ orbitals are ~0 and ~93%. The small, negative A_{iso} determined for C is attributed to a negative spin density induced by polarization in the filled s orbitals.

We have also generated and observed the ESR spectra of silver atom-acetylene complexes. Detailed analyses of the spectra reported here and those of other acetylene complexes will be reported soon.

Scheme I



Scheme II



References and Notes

(1) See, for example, a collection of review articles in *Angew. Chem., Int. Ed. Engl.*, **14**, 273 (1975).
(2) P. H. Kasai, D. McLeod, Jr., and T. Watanabe, *J. Am. Chem. Soc.*, **99**, 3521 (1977).
(3) P. H. Kasai, *Acc. Chem. Res.*, **4**, 329 (1971).
(4) P. H. Kasai and D. McLeod, Jr., *J. Chem. Phys.*, **55**, 1566 (1971).
(5) P. H. Kasai, *J. Am. Chem. Soc.*, **94**, 5950 (1972).

(6) For the analyses of hyperfine coupling tensors, see, for example, P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, Amsterdam, 1967.
(7) R. G. Barnes and W. V. Smith, *Phys. Rev.*, **93**, 95 (1954).

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On the Chemical Reactivity of Superoxide Ion

Sir:

During the past decade strong interest has developed in the chemistry of superoxide ion. Electrochemical investigations in aprotic solvents[1-6] have established that molecular oxygen is reduced by a reversible one-electron process to superoxide ion

$$O_2 + e^- \rightleftharpoons \cdot O_2^- \quad E^{\circ\prime} = -0.75 \text{ V vs. SCE} \qquad (1)$$

which in turn is reduced by a second irreversible one-electron process (with the solvent involved).[5]

$$\cdot O_2^- + e^- \rightarrow HO_2^- \quad (E_{pc})_{Me_2SO} = -2.0 \text{ V} \qquad (2)$$

Of the range of reactions for $\cdot O_2^-$ that have been described recently, two properties, its nucleophilicity[7] and its reducing power[8-11] (roughly equivalent to dithionite ion),[12] seem well-documented. On the other hand, its propensity to act as an oxidizing agent[9,13-18] is much more equivocal. Although solutions of superoxide can cause a net oxidation of substrates, we present evidence that $\cdot O_2^-$ cannot act directly as an oxidant for solution conditions where it is stable, namely aprotic media. Furthermore, although the pK_a of $HO_2\cdot$ in water has been shown to be 4.88 (i.e., $\cdot O_2^-$ is a weak base),[19] we present arguments and preliminary data to show that solutions of $\cdot O_2^-$ behave as if they are strongly basic.

Nonoxidizing Properties. Equations 1 and 2 indicate that from a thermodynamic standpoint *superoxide ion is a moderate reducing agent, but a pitifully weak oxidizing agent (roughly the equivalent of sodium ion)*.[2,5] However, in the presence of proton sources, superoxide ion disproportionates rapidly[19] to form peroxide ion and oxygen. Because all the reports that discuss the oxidizing properties of superoxide ion have involved systems with proton sources, a reasonable explanation of the observed oxidation reactions is that they actually involve products of the disproportionation reaction.[20]

The oxidative inertness of $\cdot O_2^-$ is confirmed by its nonreactivity with a wide variety of functional groups, including benzaldehyde, in rigorously aprotic solutions (dry pyridine).[22]

In support of these considerations, we have undertaken a series of studies of 3,5-di-*tert*-butyl-*o*-quinone, 3,5-di-*tert*-butylcatechol, and catechol mono- and dimethyl ethers in acetonitrile. (The catechol, in the presence of KO_2 in acetonitrile and THF, recently has been shown to be oxidized to a complex mixture of products, including the *o*-quinone.[13]) Figure 1a illustrates the electrochemical reduction of oxygen to superoxide ion (upper peak), and the reoxidation of the latter (lower peak). Reduction of $\cdot O_2^-$ does not occur at potentials less negative than those which bring about solvent reduction (ca. −2.0 V). The lower peaks of curves b and c represent the oxidation of 3,5-di-*tert*-butylcatechol and its anion (formed as described in the legend), respectively. Curve d represents the reversible reduction of 3,5-di-*tert*-butyl-*o*-quinone to its semiquinone. These results indicate that it is thermodynamically unfavorable for $\cdot O_2^-$ to oxidize the catechol or its anion in acetonitrile by direct electron transfer.

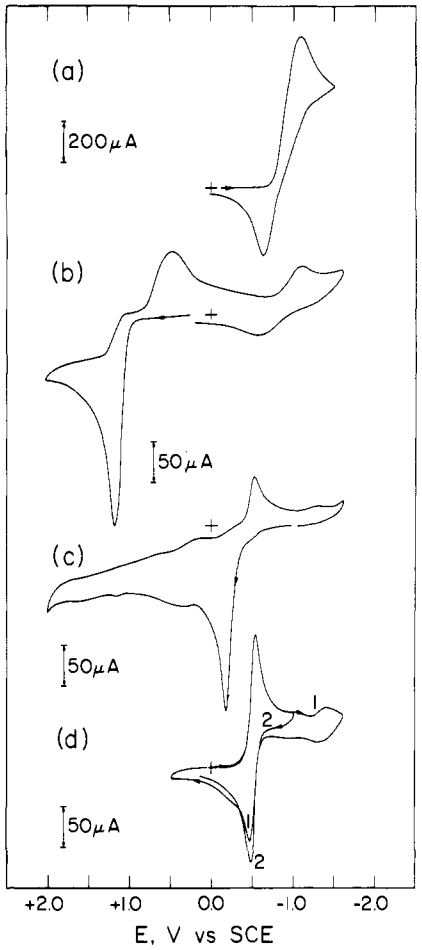
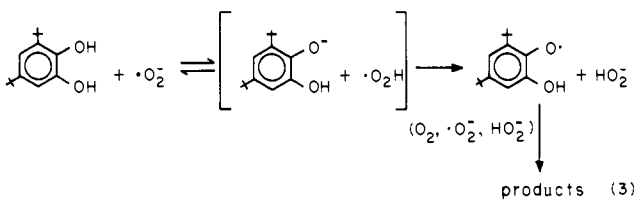


Figure 1. Cyclic voltammograms in acetonitrile that contains 0.1 M tetraethylammonium perchlorate (scan rate, 0.1 V/s at a platinum electrode (0.23 cm²)): (a) molecular oxygen at 1 atm, (b) 2 mM 3,5-di-*tert*-butylcatechol, (c) 2 mM 3,5-di-*tert*-butylcatechol plus 4 mM tetraethylammonium hydroxide, and (d) 2 mM 3,5-di-*tert*-butyl-*o*-quinone.

Indeed, we find that combining a solution of superoxide ion with 3,5-di-*tert*-butylcatechol anion in pyridine results in no reaction within 15 min. As previously reported,[2,14,15] superoxide ion reacts rapidly with the un-ionized catechol. We also find that neither the monomethyl nor the dimethyl ether of catechol reacts with $\cdot O_2^-$ to yield the quinone or semiquinone, but the former promotes the disporportionation of $\cdot O_2^-$.[20] Taken together with the electrochemical data these chemical results show that the initial reaction of superoxide with 3,5-di-*tert*-butylcatechol must be a proton transfer from catechol to the superoxide ion followed by further chemistry of the $HO_2\cdot$ so produced. Several subsequent paths to products can be envisioned. One is a cage reaction between catechol anion and $HO_2\cdot$, as depicted in eq 3, with subsequent reaction



between the semiquinone radical and any of a variety of potential further reactants. Another path, if the catechol anion becomes free, is attack by the molecular oxygen that results from disproportionation of $HO_2\cdot$ and $\cdot O_2^-$.[20,23] In this case the overall reaction would be represented by eq 4. The net reaction, starting with $\cdot O_2^-$, is then eq 5 which accounts not just for the

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