BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2723—2726 (1970)

The Effect of Adsorbed Amines on the ESR of Copper Oxide

Hisashi Ueda and Naoyuki Todo

Government Chemical Industrial Research Institute, Tokyo, 2-19-19 Mita Meguro-ku, Tokyo

(Received March 6, 1970)

The effect of several additives on the ESR of copper oxide was studied. Among the additives studied, amines and NH_3 had peculiar effects on the ESR spectra. From the spectrum formed by NH_3, it is concluded that the $(Cu\text{–}NH_3)^{2+}$ complex cation is formed on the surface of a CuO particle. The formation of this complex cation obeyed a pseudo-first-order rate and can be interpreted in terms of the surface reaction between the exposed Cu^{2+} and NH_3. Among the amines studied, only primary amines gave ESR spectra which provide evidence for the existence of $(Cu\text{-amine})^{2+}$ complex cations. The foregoing fact and the results obtained on the three isomers of chloroaniline indicate that a strong *s*-character of the lone-pair orbital is needed if an amine molecule is to occupy a surface defect of the O^{2-}, by which the Cu^{2+} is exposed on the surface, thus forming a complex cation. By these facts, the *d*-orbital of Cu^{2+}, which can overlap with the nitrogen lone pair of the amine molecule, is concluded to be d_{z^2}. The three principal values of the *g*-tensor for the $(Cu\text{–}NH_3)^{2+}$ complex cation depend greatly on the temperature, indicating that this cation has some rotational and vibrational motions below 130°C, at which point Cu^{2+} and NH_3 dissociate.

The electron spin resonances of copper complex have been studied in both the liquid and solid states.[1] The paramagnetic species, which exist only on the surfaces of particles of copper compounds, have been studied little, however. The paramagnetic species formed on the surface of CuO particles by various solid additives have been observed by one of the present authors.[2] In that work, it was found that the effect of the aromatic amines on the surface of the oxides studied is different from those of the other types of aromatic compounds. In the present report, the effect of NH_3 and a few aromatic amines on the ESR of cupric oxide is studied in order to discuss the nature of the paramagnetic species thus formed.

Experimental

The cupric oxide used was prepared by the oxidation of cupric carbonate. The adsorption of an amine on CuO particles was carried out by adding a solution of it (0.2 mM amine in 2.0 m*l* of purified benzene per 1.000 g of CuO) to copper oxide powder. After the evaporation of the solvent, the CuO-amine mixture was placed in an ESR sample tube and evacuated to 10^{-4} mmHg or to the vapor pressure of the additive. NH_3 and five other additives, used for comparison, were added in the gas phase at the pressure of 405 mmHg (N_2O), 653 mmHg (H_2), 294 mmHg (NH_3), 107 mmHg (tetrahydrofuran), 63 mmHg (benzene), and 89 mmHg (1,2-dichloroethane), all at 28.0°C.

Results

In Table 1 the relative intensities and the δH_{msl} values obtained from the ESR spectra of CuO with several additives are shown. It may be seen

---

[1] H. R. Gersman and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962); A. H. Maki and B. R. McGarvey, *ibid.*, **29**, 31 (1958).

[2] H. Ueda, This Bulletin, **43**, 319 (1970).

that only NH_3 affects the spectrum considerably and that only it yields the narrow ESR absorption in addition to the broad absorption which it yields in common with the other additives. This paper will descuss only the narrow component of the ESR spectra obtained from NH_3 and aromatic amines. In Fig. 1, a-d, the narrow components of the ESR spectra obtained from a CuO–NH_3 sample at various measurement temperatures are shown. The thermal change in the shape of the spectra is reversible in the temperature region below 140°C. When the sample is heated to as much as 300°C, the paramagnetic species (giving rise to the a–d spectra) receive some irreversible thermal damage; the resulting spectrum, measured at 20°C, is shown as e. If a CuO–NH_3 sample which is heated to 135°C (showing the *d* spectrum) is quickly cooled to 103°C, and if the spectra are repeatedly recorded, the intensity of the absorption spectrum, to be identified as I_t, begins to increase with the rate, as is shown in Fig. 2. As is shown in the figure, $\log(I_\infty - I_t)$ changes linearly with respect to time, t, indicating that the formation is a first- (or a pseudo-first-) order reaction. The spectrum (Fig. 1a) indicates three principal values of the g-factor, as has been observed with several cupric-ammonium complex salts.[3,4] The magnitude of the three principal

TABLE 1. ESR OF CUPRIC OXIDE WITH VARIOUS ADDITIVES

Additive	Relative intensity*	δH_{msl} (gauss)
None	3.38×10^5	700 ± 40
H_2	4.50×10^5	950 ± 40
NH_3, broad comp.	3.08×10^5	800 ± 40
NH_3, narrow comp.	3.60×10^3	see text
C_6H_6	2.11×10^5	730 ± 40
1,2-Dichloroethane	3.42×10^5	800 ± 40
N_2O	2.27×10^5	800 ± 40
Tetrahydrofuran	2.70×10^5	800 ± 40

* Integrated value. The average g-factor is 2.21.

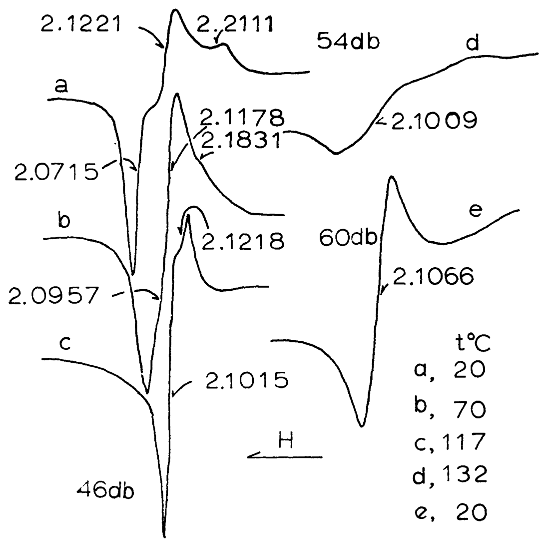

Fig. 1. The narrow component of the ESR absorption spectrum obtained from CuO-NH_3 sample. The g-factor is indicated with an arrow pointing the position on the curve. The temperature at which measurements were made are shown in the right bottom corner. The curve e is after thermal treatment at 300°C. The amount of current amplfication is shown in db.

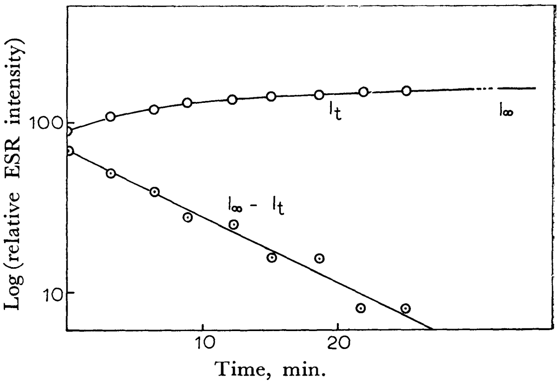

Fig. 2. The growing rate of the intensity of the narrow component of the ESR signal from a sample of CuO-NH_3 at 103°C. I_∞ is for time infinity and I_t is for time$=t$.

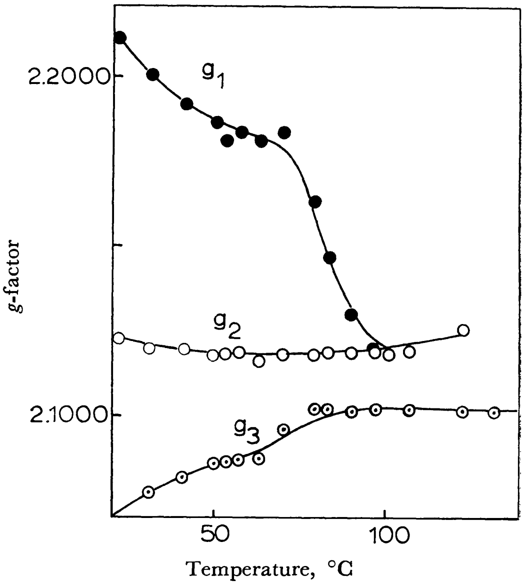

Fig. 3. The dependence of the three principal values of the g-tensor obtained by a (CuO-NH_3) sample upon the temperature of measurement.

---

3) T. Okamura and M. Date, *Phys. Rev.*, **94**, 314 (1954).

4) E. H. Carlson and R. D. Spence, *J. Chem. Phys.*, **24**, 471 (1956).

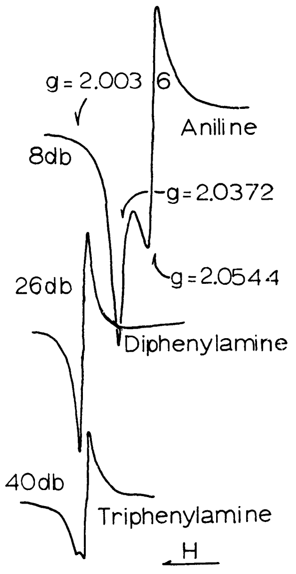

Fig. 4. The central components of the ESR spectra obtained with CuO and aromatic amines. The amount of current amplification is indicated in db. Measurements were made at 20°C.

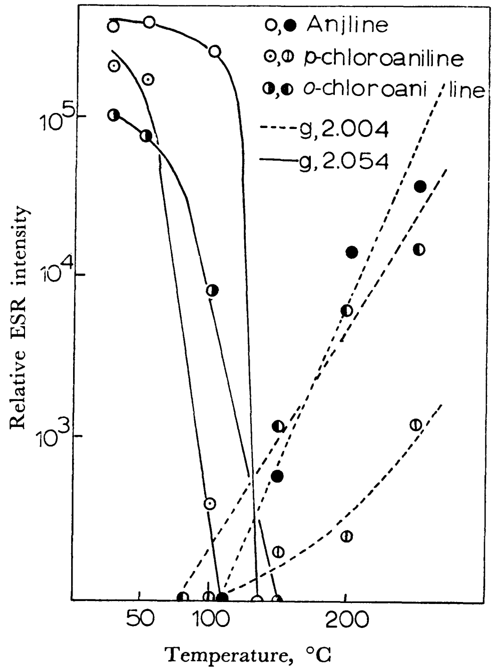

Fig. 5. The dependence of the relative intensities of the narrow ESR components of the (CuO-aromatic amine) specimens on the temperature of the thermal treatment, which is on the abscissa. Measurements were made at 20°C.

values of the g-tensor depend on the temperature of measurement, as is shown in Fig. 3. According to previous studies,[4] it seems reasonable to assign the g_1 to the $g_{\parallel}$, and the g_2 and g_3, to the $g_{\perp}$. When aromatic amines are used as additives, the ESR spectra shown in Fig. 4 are observed. Only primary amines, aniline, *o*- and *p*-chloroanilines but not *m*-chloroaniline, give spectra which are identical. In Fig. 5 the temperature dependence of the ESR intensities obtained by aniline and isomeric chloroanilines are shown.

Discussion

The ratio between the area covered by the narrow component of the spectrum obtained in the CuO–NH_3 sample at 29°C and the broad component of the same spectrum is approximately 0.0117, as may be seen in Table 1. If the surface Cu^{2+} is all converted to $(Cu–NH_3)^{2+}$-type complex ions, and if all the other Cu^{2+} (the second and the inner layers under the surface of a CuO particle) are not affected, the above-mentioned ratio can be shown to be a function of the dimensions of the particles. If the formation of $(Cu–NH_3)^{2+}$ is limited to some particular Cu^{2+} points on the surface, or if some of the Cu^{2+} are completely covered by O^{2-} ions, the ratio (the surface Cu^{2+} to combine with NH_3)/(the total surface and bulk Cu^{2+}) becomes smaller than expected. The observed ratio of the two spectral components is not unreasonable for considering the formation of $(Cu–NH_3)^{2+}$ exclusively at some or all of the surface Cu^{2+} points.

The reaction rate, $Cu^{2+}+NH_3 \rightarrow (Cu–NH_3)^{2+}$, also indicates that this is a surface process. The reaction rate is proportional to the product of the concentrations, $[Cu^{2+}][NH_3]$. If the reaction occurs under the surface, the $[NH_3]$ will be controlled by the velocity of the penetration of NH_3 into and through the CuO particles and will not depend much on the time, for the pressure of NH_3 is constant. $[Cu^{2+}]$ will also be constant, and the reaction rate will be zeroth order. However, if the reaction on the surface is assumed, $[NH_3]$ or p_{NH_3} is constant because of its excess amount, and $[Cu^{2+}]=[Cu^{2+}]_{total}-[(Cu–NH_3)^{2+}]$, where $[Cu^{2+}]_{total}$ signifies the amount of Cu^{2+} on the surface prior to the introduction of NH_3. The rate of the formation of $(Cu–NH_3)^{2+}$ is equal to the rate of the decay of the surface Cu^{2+}, therefore, it proceeds with a pseudo-first-order rate. Therefore, the surface reaction model agrees well with the observed rate.

The results in the previous paper indicated that, in the case of alumina, the chemisorption occured between the p-orbitals of the oxygen anions and the π-orbital of the aromatic additive, both having the same symmetry. In contrast with it, the chemisorption in the case of CuO was considered to occur between the 3d orbital of Cu^{2+} and the additive. Acturally, in some cases the unpaired electron was found on both Cu^{2+} and the nitrogen of the additive molecule.[2] If all the surface d-orbitals of Cu^{2+} are occupied or covered by O^{2-}

ligands, there will be no way for a NH_3 to occupy or overlap with one of them. Therefore, it can be concluded that the $(Cu–NH_3)^{2+}$ complex is formed when a NH_3 molecule fills the defect of a O^{2-} ligand on the surface. As NH_3 is a neutral molecule and so has no net negative charge on it, this chemisorption will partly consist of the formation of a covalent bond between the Cu^{2+} and NH_3, and partly of a polarization of the lone-pair orbital of the NH_3 toward the Cu^{2+}. In the case of aromatic amines, only primary amines gave ESR spectra with $g=2.03$—2.06. In the case of secondary and tertiary amines, the lone pair of the nitrogen will possess a considerably more *p*-character than that of aniline. Therefore, the stronger *s*-character of the lone pair bond is the better for a foreign ligand to occupy the O^{2-} defect on the surface. Since the H–N–H angle in NH_3 is 107.3°5,6) and deviates somewhat from the pure sp^3 angle of 109°28′, the lone pair of NH_3 has a small *p*-character.

Though the *g*-factors observed in the CuO-aniline sample are closer to those of DPPH than those of the CuO–NH_3 sample, it is certain that the unpaired electron is on both Cu^{2+} and aniline; in other words, the $(Cu\text{-aniline})^{2+}$ complex is formed. The temperature dependence of the intensity of the line with $g=2.054$ is also similar to that of the $(Cu–NH_3)^{2+}$ complex (Fig. 5), and they both disappear above 130°C. In the cases of *o*- and *p*-chloroanilines, the double-bond character of C–Cl induces some negative electron density on the carbon atom to which the NH_2 group is attached. Probably because of the electrostatic repulsion, the configuration in which the nitrogen lone pair is out of the C_6H_4-plane is avoided and the *s*-character of the lone pair is strong. In the case of *m*-chloroaniline, the negative electron densities are distributed on the carbon atoms next to the $\rangle C–NH_2$ group; probably for this reason the nitrogen lone pair possesses some *p*-character of overlapping with the molecular π-bond.

As the O^{2-} ions are in the tetrahedral directions with respect to Cu^{2+},7) the defect of one of the four O^{2-} ligands surrounding one Cu^{2+} ion leads to a electrostatic field of the C_{3v} symmetry. In the T_d symmetry, the unpaired electron occupies one of the ^2E_g orbitals, *i.e.*, x^2–y^2 and z^2. If the symmetry goes down to C_{3v}, it is uncertain which orbital accommodates the unpaired electron. The experimental evidence that the foreign or amine ligand orbital has a strong *s*-character suggests that the corresponding Cu^{2+} orbital has an A_1 symmetry or z^2. As the electronic state of a Cu^{2+} is considered to consist of a hole in a completely-filled 3d-shell, the energy eigenvalue of the z^2 orbital without an O^{2-} in the *z*-direction will be higher than that with an O^{2-}. Thus, it is possible that the energy level of the orbital with A_1 symmetry eventually becomes higher than those of the other orbitals with E symmetry when the crystal field symmetry goes down to C_{3v}. Therefore, for this reason too, it is likely that the unpaired electron occupies the z^2 orbital. The molecular orbitals formed may be written as $k\cdot z^2+l\cdot\phi_{\sigma N}$ where k and l are coefficients to be determined by the relative weights of the spin densities in each orbital.

The relatively smaller *g*-factor of $(Cu\text{-aniline})^{2+}$ absorption is due to the greater polarizability of the $H–C_6H_4–NH_2$ bonds toward Cu^{2+} than that of $H–NH_2$ bonds toward Cu^{2+}; as a result, the l for aniline is larger than that for NH_3. As the unpaired electron is in an antibonding molecular orbital with coefficients (k and $-l$), the larger l value for $(Cu\text{-aniline})^{2+}$ makes the complex less stable and the *g*-factor closer to that of DPPH.

The temperature dependence of the *g*-factor in Fig. 3 indicates that the three components of the *g*-factor at relatively low temperatures are reduced to two components at higher temperatures. This is due to the rotational and vibrational motion of the Cu^{2+}–NH_3 (partially covalent) bond. The anisotropy in the *g*-tensor is averaged out by thermal motions at elevated temperatures. Somewhere above 140°C, but below 300°C, the surface Cu^{2+} species decompose or react irreversibly with NH_3 and yield some paramagnetic species which give the ESR spectrum shown in Fig. 1e.

The active site of a solid catalyst may be described in two ways. One is in terms of the geometrical positions at which they are located on the surface of a particle, while the other is a description in molecular- or atomic-orbital language. The geometrical problems can be studied by means of an electron microscope and other optical techniques. The bulk symmetry of the orbitals and the crystal field in the solid state can be studied by X-ray and other methods. The symmetry of the atomic- or molecular-orbitals or crystal field on the surface, however, has not been investigated much. From such a point of view, the method employed in the present work would seem to have some significance even when the catalytic importance of CuO is considered to be rather meager.

---

5) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," van Nostrand Co., New York, N. Y. (1945).

6) M. T. Weiss and M. W. P. Strandberg, *Phys. Rev.*, **83**, 567 (1951).

7) R. Kiriyama, "Kozomukikagaku," Vol. 1, Kyoritu Publ. Co., Tokyo (1958), p. 110.