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EPR Study of the Oxidative Coupling Reaction of Aniline Homogeneously Catalyzed by $Cu(C_5H_5N)_4(NO_3)_2$

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EPR has been used to study the oxidative coupling reaction of aniline, resulting in azobenzene, catalyzed in homogeneous phase by $Cupy_4(NO_3)_2$ (py = pyridine). Addition of aniline to the catalytic complex results in the progressive reduction of Cu(II) to Cu(I) which, in turn can be reoxidized. The Cu^{2+}–Cu^+ redox couple hence plays an important role in the reaction.

An intermediate radical species is observed. Its structure is proposed to be C_6H_5—N°=O^+, i.e., a radical cation produced by partial oxidation of aniline. In this radical, the unpaired electron is almost exclusively localized on nitrogen and it has a predominant $2p_z$ character. The mechanism which is proposed for the oxidative coupling reaction differs from the original mechanism put forward by Kinoshita.

INTRODUCTION

Turkevich, Ono and Soria (*1*) suggested in a recent discussion of the properties of the Cu–pyridine complex stabilized in Y-zeolite that "it would be of interest to investigate the catalytic properties of this complex since the Cu(II)-pyridine system has been reported to be a good catalyst for homogeneous oxidation (*2*)." A particular type of oxidation reaction catalyzed by this complex is the so-called oxidative coupling of acetylenic compounds (*3*), phenols (*4*), or aniline (*5*), resulting in the formation of new organic compounds and linear polymers.

Although the overall reaction scheme is very simple:

$$2\,R\text{-}H + \tfrac{1}{2}\,O_2 = R\text{-}R + H_2O, \qquad (1)$$

very few authors have proposed a mechanistic description for the reaction steps and for the role of copper (*6*, *7*). Most of the mechanisms are exclusively based on kinetic data and no detailed investigations have been reported on the search for free radical intermediates or unusual valency states of the copper ions.

This paper reports such observations in the particular case of the oxidative coupling reaction of aniline in the homogeneous phase, i.e., in ethanol solution, using as a catalyst the complex $Cu(C_5H_5N)_4$-$(NO_3)_2$. The overall reaction is then:

$$2\,C_6H_5\text{—}NH_2 + O_2 = C_6H_5\text{—}N\text{=}N\text{—}C_6H_5 + 2\,H_2O. \qquad (2)$$

This paper is restricted to the presentation of the data relevant for the understanding of the mechanism and of the catalysis. The stereochemistry of the catalytic complex,

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TABLE 1

EPR PARAMETERS OF $Cu(C_5H_5N)_4(NO_3)_2$–ANILINE MIXTURES IN ETHANOL AS A FUNCTION OF M/C[a]

M/C	$g_{\parallel}$[b]	$g_{\perp}$[b]	$A_{\parallel}^{Cu}$ (Oe)	$A_{\parallel}$(N) (Oe)	$A_{\perp}$(N) (Oe)	α^2	Relative intensity
0	2.260	2.068	176	9.5	13	0.78	1
10	2.244	2.068	177	—[c]	13	0.77	—
30	2.234	2.061	175	—[c]	14	0.75	—
100	2.231	2.061	175	—[c]	13	0.75	0.03
500	—[d]	—[d]	—[d]	—[cd]	—[d]	—[d]	<0.01
500 + oxygen	2.214	—[e]	—	—	—	—	1

[a] All spectra recorded at X-band and 77°K.

[b] All values within ±0.003.

[c] No visible superhyperfine structure.

[d] No Cu^{2+} observed (see text for free radical EPR parameters).

[e] Broad line, $g_{\perp}$ position undetermined.

its electronic and dynamic structure have been discussed elsewhere (*15–19*).

EXPERIMENTAL METHODS

Materials

The catalyst, $Cupy_4(NO_3)_2$ (py = pyridine), was prepared very simply by addition of pyridine in excess to a $Cu(NO_3)_2$ solution in absolute ethanol. After filtration and drying, the stoichiometry of the complex was confirmed by chemical and thermogravimetric analyses.

Pyridine and aniline were freshly distilled before use. EPR samples were prepared by dissolving a known amount of complex in absolute ethanol so as to obtain a 10^{-2} M solution and by adding various amounts of aniline. The samples are characterized by the ratio M/C, the molar ratio of reactant to catalyst.

Instrumental Techniques

EPR measurements were made on an X-band E-12 Varian spectrometer, using 100 kHz modulation and at 77°K, i.e., on the frozen sample solutions.

RESULTS

Table 1 summarizes most of the EPR data while Figs. 1, 2 and 3 represent typical spectra observed for M/C ratios equal respectively to 0, 100, and 500. In Table 1, the reported nitrogen superhyperfine coupling constants, $A_{\parallel}$(N) and $A_{\perp}$(N), are the experimental values measured, respectively, on the $g_{\parallel}$ and $g_{\perp}$ parts of the spectra. For the type of complex which we studied correct values are given by $A_{\parallel}^{N} = A_{\perp}(N)$ and $A_{\perp}^{N} = \frac{1}{2}[A_{\parallel}(N) + A_{\perp}(N)]$. These have

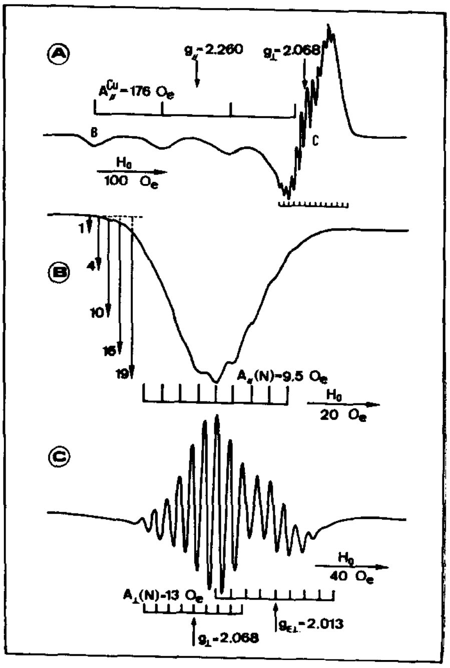

FIG. 1. EPR spectrum at 77°K (X-band) of a 10^{-2} M solution of $Cu(C_5H_5N)_4(NO_3)_2$ in ethanol: (A) overall spectrum. (B) detail of the $m_I = -3/2$ $g_{\parallel}$-component. (C) second derivative spectrum of the $g_{\perp}$ feature.

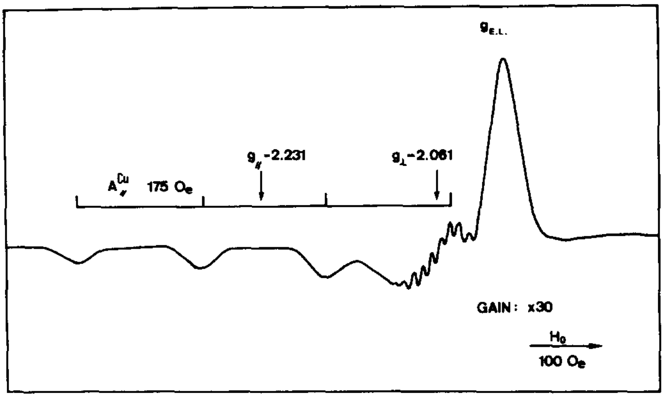

FIG. 2. EPR spectrum at 77°K (X-band) of a 10^{-2} M solution of $Cu(C_5H_5N)_4(NO_3)_2$ in ethanol: (aniline)/(complex) = $M/C = 100$.

not been calculated as the $A_{\|}(N)$ value has been resolved in only one case ($M/C = 0$).

The relative gains of the spectra represented in Figs. 2 and 3 are, respectively, higher by a factor of 30 and near 100 than that used for the spectra represented in Fig. 1. Hence, it is clear from the sequence of Figs. 1 to 3 that the addition of aniline drastically alters the spectrum of the Cu (II)-pyridine catalytic complex. The spectral intensity is decreased by a factor of 30 for $M/C = 100$ (Fig. 2) and is only of nearly 1% of the original intensity for $M/C = 500$ (Fig. 3). If the latter system is exposed to air, or if oxygen is passed into the solution, the original spectral intensity is quickly restored as shown in Fig. 4.

The small intensity and particular spectrum shown in Fig. 3 is only observed when the addition of aniline is made in quasi-oxygen-free conditions (note that there is some residual oxygen in the system provided by the solvent).

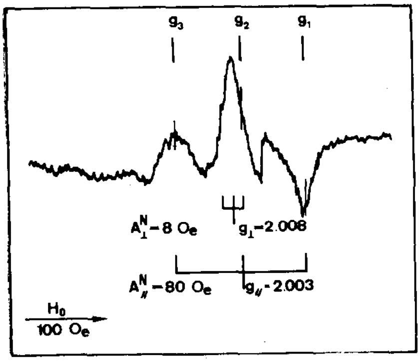

FIG. 3. EPR spectrum observed at 77°K (X-band) for a 10^{-2} M solution of $Cu(C_5H_5N)_4 \cdot (NO_3)_2$ in ethanol and $M/C = 500$.

Electronic spectra of the pure complex in solution show bands at about 13,800 cm^{-1} ($\Delta E_{3z^2-r^2}$), 15,650 cm^{-1} (ΔE_{xy}) and 25,000 cm^{-1} (ΔE_{xy}), hence giving approximate values for the splittings of the A_{1g}, B_{2g}, and E_g levels from the ground state B_{1g}. Upon addition of aniline, the absorption maximum at 15,650 cm^{-1} was progressively shifted up to near 16,800 cm^{-1}.

DISCUSSION

The spectrum shown in Fig. 1, corresponding to the pure catalyst $Cupy_4(NO_3)_2$, is very similar to that reported for the Cu(II)-pyridine complex in Y-zeolite (*1*, *15*). However, in addition to the four hyperfine lines due to the $I = 3/2$ nuclear spin of Cu ($A_{\|}^{Cu} = 176$), a superhyperfine structure of nine lines is readily distinguished on the $m_I = -3/2$ component of the $g_{\|}$ feature, Fig. 1B. These lines have approximate intensity ratios of 1:4:10:16:19:16:10:4:1, and result from the interaction of the unpaired electron spin (from Cu^{2+}) with four equivalent nitrogen nuclei ($I^N = 1$) provided by the four pyridine ligands. The second derivative spectrum of the high field region (Fig. 1C) shows 15 lines which result from superposition of

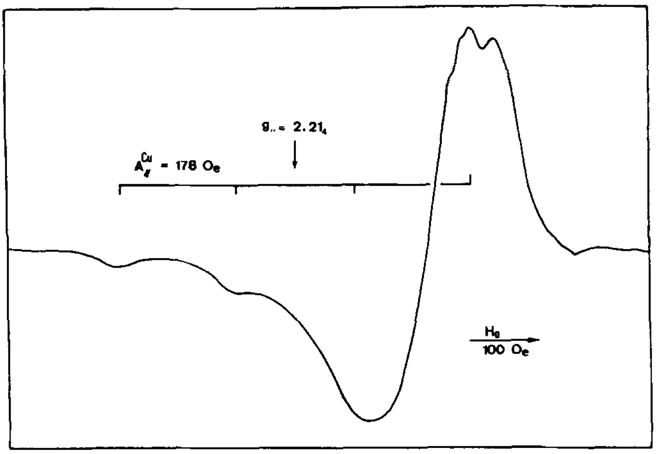

FIG. 4. EPR spectrum at 77°K of the $M/C = 500$ mixture after passing O_2 at 300°K for 5 min.

two nine line patterns, with similar intensity ratios, centered, respectively, on $g_{\perp}$ and g_{EL} [The latter corresponds to an "extraneous line" as first discussed by Neiman and Kivelson (*10*)]. On the basis of the EPR parameters and of the electronic spectra, knowing that the four ligand nitrogens are equivalent, and by analogy with previous work (*1*, *17*, *18*, *19*), it is concluded that the effective symmetry of this $Cupy_4^{2+}$ chromophore is D_{4h}. Hence the catalytic entity, the $Cupy_4^{2+}$ ion, may be assumed as a first approximation and for the sake of simplicity to be square planar.

From the variation of the spectral intensity as a function of the M/C ratio, it is immediately concluded that the addition of aniline in the absence of excess oxygen to the Cu(II)-pyridine complex results in its progressive reduction to a Cu(I) complex which is not paramagnetic. The easy reoxidation of the latter by O_2 establishes that the oxidative coupling reaction of aniline involves the Cu^{2+}–Cu^{+} redox couple, the catalytic complex being in the first step reduced by the organic reactant. A similar conclusion was also put forward for the phenylacetylene oxidative coupling catalyzed by the same complex (*8*).

Quantitative conclusions on the behavior of the Cu(II) species, initially $Cupy_4^{2+}$, can be drawn by taking a closer look at the values reported in Table 1. Quite obviously:

1. A progressive change occurs in the characteristic EPR parameters of the Cu(II) species as the M/C ratio is increased;
2. The values of α^2 decrease for increasing M/C ratios, which means, according to the theory of Neiman and Kivelson (*9*), that the covalent character of the Cu–N bonds is reinforced;
3. The observed g-values also decrease for increasing M/C ratios; the magnitude of this effect cannot be interpreted only by the variation in α^2 and hence it shows an increase in the spacing of the E_g (d_{xz} and d_{yz} orbitals) and B_{2g} (d_{xy} orbitals) levels with respect to the B_{1g} ground state ($d_{x^2-y^2}$ orbital). This is confirmed by the electronic spectra data.

Of special interest is the spectrum observed for $M/C = 500$, in quasi-oxygen-free conditions. It does not correspond to a Cu^{2+} species.

Three lines are observed which are, respectively, centered at $g_1 = 1.953$, $g_2 = 2.000$, and $g_3 = 2.053$, suggesting that this spectrum might correspond to a radical-type species. Comparison of these data with literature values (*11*) shows that it is not a peroxy-type radical. The overall shape of the EPR signal and its symmetry with respect to the central line suggest that it could be a triplet, the three lines arising from hyperfine coupling of the unpaired electron with the $I = 1$ nuclear spin of nitrogen; hence, this radical probably derives from aniline. However, no proton hyperfine splittings are observed in addition to the former structure, which indicates that the unpaired electron is not coupled to nearby protons, and it must be kept in mind that some oxygen is needed to observe it (residual oxygen in the system). This spectrum shows several similarities with that of the nitrobenzene radical anion (*12*), and in view of the former arguments it is tempting to attribute our spectrum to the $(C_6H_5{-}N^{\bullet}{=}O)^+$ radical cation that could be formed as an intermediate during the oxidative coupling reaction of aniline [see Eq. (5)].

The spectrum is then readily analyzed using the procedure of Fox, Gross and Symons (*13*). The lines at $g = 1.953$ and $g = 2.053$ are the outer hyperfine features (due to the coupling with the $I = 1$ spin of nitrogen) of the component parallel to the field. The middle hyperfine line expected for this component, at 2.003, along with the three perpendicular features are apparently contained within the broad central signal at $g_2 = 2.000$. Based on the line shape of this central signal, further analysis gives the approximate following values: $g_\perp \cong 2.008$ and $g_\parallel = 2.003$ with $A_\parallel{}^{N} \cong 80$ Oe and $A_\perp{}^{N} \cong 8$ Oe. The hyperfine tensor of nitrogen-14 can then be resolved into an isotropic part and an anisotropic part in the form:

$$\begin{vmatrix} A_\perp & & \\ & A_\perp & \\ & & A_\parallel \end{vmatrix} = A_{\mathrm{iso}} + \begin{vmatrix} -B & & \\ & -B & \\ & & 2B \end{vmatrix} \qquad (3)$$

The only reasonable solution proves to be $A_{\mathrm{iso}} = 32$ Oe and $2B = 48$ Oe. In order to calculate the spin densities in the $2s$ and $2p_z$ orbitals of the nitrogen atom of this radical, one may compare the values of A_{iso} and $2B$ with the theoretical values obtained for the odd spin being completely in either a $2s$ or a $2p_z$ orbital (*14*). Hence, one finds that the unpaired electron is quite exclusively on the nitrogen atom, having about 5% $2s$ character and 95% $2p_z$ character. The unpaired electron must then be largely localized in a p_z orbital. This orbital is perpendicular to the plane of the molecule.

The identification of a possible radical intermediate such as $(C_6H_5{-}N^{\bullet}{=}O)^+$ leads us to propose the following mechanism for the oxidative coupling reaction of aniline on $\mathrm{Cupy_4(NO_3)_2}$:

$$\underset{\text{(I)}}{\mathrm{Cupy_4^{2+}}} + \mathrm{C_6H_5NH_2} \rightleftharpoons \underset{\text{(II)}}{\mathrm{Cupy_3^{+}(C_6H_5NH_2^{\cdot})^{+}}} + \mathrm{py}, \qquad (4)$$

$$\mathrm{Cupy_3^{+}(C_6H_5NH_2^{\cdot})^{+}} + \mathrm{O_2} \rightleftharpoons \underset{\text{(III)}}{\mathrm{Cupy_3^{+}(C_6H_5N^{\cdot}{=}O)^{+}}} + \mathrm{H_2O}, \qquad (5)$$

$$2\,\mathrm{Cupy_3^{+}(C_6H_5N^{\cdot}{=}O)^{+}} + 2\,\mathrm{py} \rightarrow 2\,\mathrm{Cupy_4^{2+}} + \mathrm{O_2} + \underset{\text{(IV)}}{\mathrm{C_6H_5{-}N{=}N{-}C_6H_5}}. \qquad (6)$$

It is assumed in this scheme that the radical stays coordinated to the central copper ion. This is not necessary for the reaction to proceed: coupling of two radical cations could as well occur in solution. Note, however, that a localization of the odd spin in the $2p_z$ nitrogen orbital would be favored if the radical is coordinated to Cu^+. Indeed, the bonding of aniline to Cu^{2+} occurs in this scheme by overlap and electron transfer from the $2p_z$ lone pair orbital of nitrogen (aniline) to the $d_{x^2-y^2}$ orbital of Cu^{2+}. Hence, the unpaired electron in (II) as well as in (III), the radical of interest, will be strongly stabilized in the $2p_z$ orbital of nitrogen; this in agreement with the EPR data.

Species I and III have been observed by EPR in this study. Adducts of type II have not been observed: Cu^+ is not paramagnetic and the aniline radical is probably very reactive and then in very small concentration. We have also observed that the addition of azobenzene (IV) did not affect the EPR spectrum of the fresh catalyst. Hence Eq. (4) explains the progressive decrease in spectral intensity for increasing M/C ratios and Eq. (5) is a possible mechanism for the formation of the observed radical cation. Equation (6) must be irreversible as azobenzene has no effect on the $\mathrm{Cupy_4^{2+}}$ complex. It is important to note that in the mechanism we propose, by contrast to that put forward by Kinoshita (*5*), the oxygen consumption is not due to the reoxidation of Cu^+ to Cu^{2+} but to a reaction with the unstable $(C_6H_5NH_2^{\bullet})^+$ radical.

Work is in progress to study the catalytic behavior of the same complex localized in the supercage of Y-type zeolite.

CONCLUSIONS

The present study shows quite unambiguously that:

1. during the catalytic oxidative coupling reaction of aniline to $Cupy_4(NO_3)_2$ in the homogeneous phase, a radical is formed for which a possible structure is $(C_6H_5—N^{\bullet}=0)^+$; this radical is a reaction intermediate in which the odd spin localized on nitrogen has mostly $2p_z$ character;
2. addition of aniline to the catalytic complex results in the progressive reduction of Cu(II) to Cu(I), in quasi-oxygen-free atmosphere, thereby confirming the role played by the Cu^{2+}–Cu^+ redox couple.

A mechanism is proposed which differs from the mechanism previously discussed by Kinoshita (*5*).

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