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ESR Study of Cationic Radicals in Aromatic Compound–Cu–$AlCl_3$ Systems

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The electron spin resonance spectra of several aromatic compound–Cu–$AlCl_3$ systems were observed. When benzene, toluene, and ethylbenzene were used as the aromatic compounds, a singlet with a g-value of 2.003 was obtained. In the case of the *o*-, *m*-, and *p*-xylene systems, spectra with well-resolved hfs's resulted. It was suggested that cationic radicals were formed by a transfer of an electron from the benzene ring to Cu(II)–$AlCl_3$.

It has been reported that copper(I) chloride, aluminium chloride, and benzene form a ternary complex, and its structure has been determined by an X-ray diffraction technique.[1] The copper(I) ion has a distorted tetrahedral environment and is located above one of the C–C bonds of the benzene ring by means of a π-type interaction. The distances between the copper(I) ion and the two nearest adjacent carbon atoms are not equivalent; they are 2.15 and 2.30 Å respectively.

When the complex was used in the Friedel-Crafts reaction as a catalyst, the product distribution differed from that in the reaction catalyzed by aluminium chloride alone.[2] For example, in the synthesis of cymene from toluene and isopropyl chloride, the selectivity in *o*- and *m*-products was highly increased by use of the complex. However, the catalytic action of the complex has not been discussed in detail, and it seemed that it would be interesting to study the nature of the aromatic compound–Cu–$AlCl_3$ system (ArH–Cu–$AlCl_3$) by means of the ESR technique from the viewpoint of the interaction of copper with a benzene ring.

Experimental

Materials. The aromatic compounds were carefully purified by the usual method. The anhydrous copper(I) chloride and copper(II) chloride were prepared by the reduction of, and by the dehydration of copper(II) chloride dihydrate respectively. Commercial G. R. grade copper(I) oxide, copper(II) oxide, and aluminium bromide were used without further purification. The aluminium chloride was purified by the sublimation of a commercial G. R. grade reagent.

Preparation of the Samples. The samples were prepared in the following two ways.

Method A: In a 50-ml reaction flask, a mixture of known amounts of copper salt, aluminium salt, and a 5-ml portion of an aromatic compound was stirred under a nitrogen atmosphere at room temperature. The upper layer was put into an ESR sample tube by means of a syringe, and the tube was sealed.

Method B: In a 10-ml reaction vessel equipped with an ESR sample tube, known amounts of copper salt and aluminium salt were placed, and then the vessel was evacuated. About a 5-ml portion of a degassed aromatic compound was distilled into the vessel by the use of a vacuum line, after which the mixture was stirred. An upper layer was decanted into the sample tube and sealed. The concentration of copper salts was 0.1—0.2 mol/l.

ESR Spectra. The electron spin resonance spectra were usually recorded at room temperature with a JEOL-JESPE spectrometer, while the g-values were determined by the use of Mn^{2+} as a standard marker. When the measurements at an elevated temperature were necessary, the temperature was maintained by passing hot air through the cavity.

Results and Discussion

ESR Spectra of the Samples Prepared by Method A. While copper salts were insoluble in aromatic compounds, such as benzene or toluene, they were easily dissolved by the addition of aluminium chloride to form brown, purple, yellow, or green homogeneous solution. The rate of the dissolution of copper salts in the aromatic compounds increased in the order of benzene, toluene, ethylbenzene, and *p*-xylene. Copper(II) chloride was the most soluble among the copper salts used.

From Table 1 one can see that all the spectra of ArH–Cu–$AlCl_3$ consist of a singlet with a g-value of 2.003 and a ΔH_{msl} value smaller than 10 G, indicating the presence of organic radicals. However, the aluminium bromide systems investigated showed no signal or, if any, a very weak one. In all cases, no spectrum due to the copper(II) ion was observed; this suggests that copper is in the copper(I) state.

Table 1. ESR spectra of aromatic compound–Cu–Al systems prepared by method A

Aromatic compound	Al-salt	Cu-salt	ΔH_{msl}/G	g-Vlaue
Benzene	$AlCl_3$	CuCl	9.00	2.003
		Cu_2O	9.45	2.003
		$CuCl_2$	7·17	2.003
		CuO	9.46	2.003
	$AlBr_3$	CuCl		2.003[a]
		CuO	—	—
Toluene	$AlCl_3$	CuCl	8.00	2.003
		Cu_2O	8.80	2.003
		$CuCl_2$	7.80	2.003
		CuO	7.50	2.003
	$AlBr_3$	CuCl	—	—
p-Xylene	$AlCl_3$	CuCl	8.10	2.003
	$AlBr_3$	CuCl	—	—
		CuO	—	—
Ethylbenzene	$AlCl_3$	CuCl	5.00	2.003

a) very weak

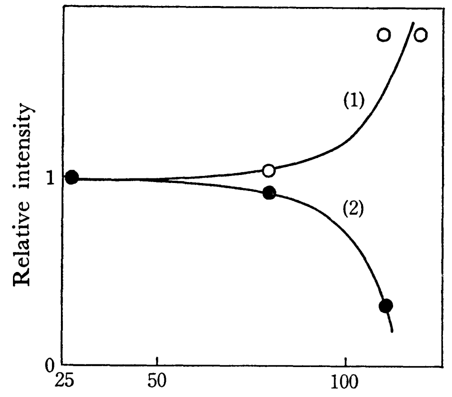

Fig. 1. Temperature dependence of the spectra of (1) toluene-CuCl-AlCl$_3$ and of (2) p-xylene-CuCl-AlCl$_3$.

Figure 1 shows an effect of the temperature on the intensities of the signals of ArH–Cu–AlCl$_3$. The ordinate indicates the intensity relative to that of the Mn^{2+} marker. The intensity of the signals of p-xylene system does not decrease up to 80 °C, while that of the toluene system increases by heating up to 120 °C. These facts indicate that the radicals are thermally stable to a considerable extent.

They were also found to be stable toward oxygen, and the radical nature still remained under an atmospheric condition when the unreacted aromatic compound was excluded. For example, when excess p-xylene was removed by the evaporation from the p-xylene–CuCl–AlCl$_3$ system, the spectrum of the residual solid material was observed to be as is shown in Fig. 2.$^{3)}$ A sharp singlet with a g-value of 2.003 is superimposed upon the broad spectrum of the copper(II) ion. It seems that the copper(II) ion was formed by the oxidation of the copper(I) ion by air during the procedure.

ESR Spectra of the Samples Prepared by Method B. As has been mentioned above, the spectra of ArH–Cu–AlCl$_3$ prepared by Method A had no hfs. This may be due to dissolved oxygen, which causes the line broadening of the spectrum. Dissolved oxygen may also affect the valence state of copper; the copper(I) ion may be oxidized to the copper(II) state during the preparation of the samples. Therefore, the effect of oxygen was excluded by preparing the samples under a vacuum. The aromatic compounds used were toluene, o-, m-, and p-xylene, while the copper salts used were copper(I) chloride, copper(II) chloride, and copper(II) oxide.

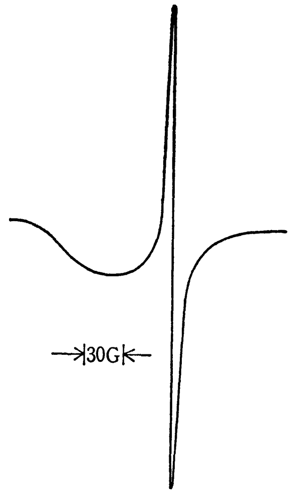

Fig. 2. ESR spectrum of p-xylene–CuCl–AlCl$_3$ after evaporation of excess p-xylene,

Copper(I) chloride, although dissolved rapidly in these organic solvents to form brown homogeneous solutions, showed no spectrum. On the other hand, spectra were obtained in all cases where copper(II) salts were used. However, the spectra of the samples prepared in toluene consisted of only a singlet; the same result was obtained in the case of p-xylene–CuCl$_2$–AlCl$_3$.

The p-xylene–CuO–AlCl$_3$ system gave a dark purple solution; its ESR spectrum, consisting of about eighty lines spaced over thirty gauss, is shown in Fig. 3. As has been mentioned before, Turner has reported that the benzene–CuCl–AlCl$_3$ complex has a π-type copper-benzene ring interaction and that the copper is located above one of the C–C bonds.$^{1)}$ Taking this into consideration, it appears that the spectrum shown in Fig. 3 is due to a cationic or an anionic radical of Turner's type. If the radical has a symmetrical configuration, and if all the protons on the benzene ring are equivalent, its spectrum will consist of thirty-five lines. An alternate explanation for the unusual complex spectrum may be that there exists a dimer of the ionic radical, as has been reported for a cationic radical of naphthalene.$^{4)}$ However, the exact assignment of the observed spectrum has not yet been done. This radical was stable in the presence of oxygen. Though line broadening occurred after air was introduced, the hfs could still be observed. The line broadening may be explained by the dipole-dipole interaction with oxygen and/or with the copper(II) ion formed by the oxidation of the copper(I) ion.

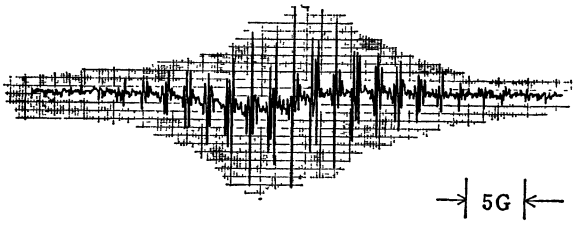

Fig. 3. ESR spectrum of p-xylene–CuO–AlCl$_3$.

Figures 4 and 5 show the spectra of o-xylene–CuO–AlCl$_3$ and m-xylene–CuO–AlCl$_3$ respectively. They are different from that of p-xylene–CuO–AlCl$_3$; each consists of about one hundred and fifty lines. It is expected that the hfs of the toluene system as well as of the other systems listed in Table 1 can be obtained by choosing optimum conditions for the preparation of these samples.

The copper(I) systems prepared by Method B yielded no signal. However a signal began to appear when air was introduced into p-xylene–CuCl–AlCl$_3$,

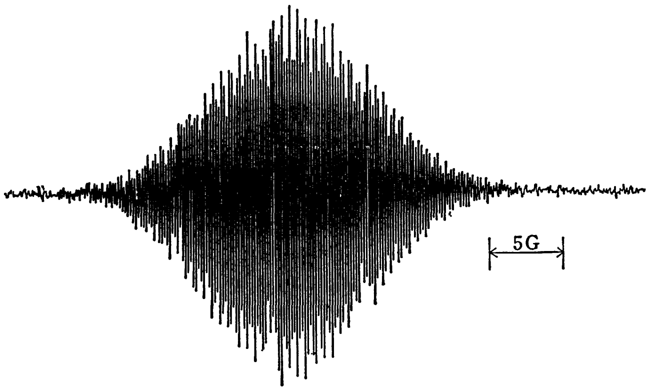

Fig. 4. ESR spectra of *o*-xylene–CuO–$AlCl_3$.

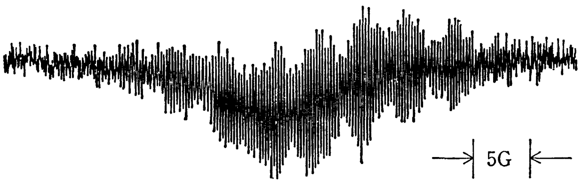

Fig. 5. ESR spectrum of *m*-xylene–CuO–$AlCl_3$.

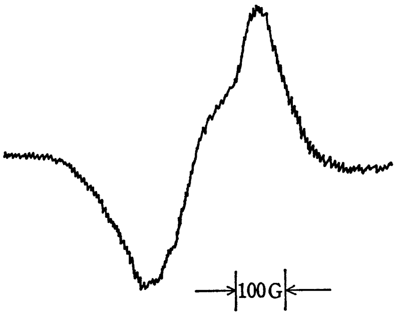

Fig. 6. ESR spectrum of *p*-xylene–CuCl–$AlCl_3$ after an introduction of air and successive addition of tetrahydrofuran.

and, in the presence of an optimum amount of air, a spectrum exactly identical with that shown in Fig. 3 was observed. On the addition of tetrahydrofuran to the system, a precipitate appeared. As is shown in Fig. 6, the spectrum of this precipitate had no signal due to an organic radical; instead, an absorption due to the copper(II) ion was observed. These results suggest that the copper ion in the system is in the copper(I) state and that the copper(II) ion is necessary to produce the organic radical. Therefore, it appears that a transfer of an electron from the benzene ring to the copper(II) ion occurs and that, as a result, the copper(I) ion and an aromatic cationic radical are formed.

It has been known that aluminium halides form complexes with aromatic hydrocarbons.[5–7] Therefore, aluminium chloride alone was dissolved in *p*-xylene under the conditions described in Method B; the spectrum of the resultant pale yellow solution was observed to be as is shown in Fig. 7. The spectrum consists of about sixteen lines, with a hyperfine coupling constant of 1.7 G. The ESR spectra of cationic radicals in the complexes of aluminium chloride with aromatic compounds (–anthracene, chrysene, and perylene–) were observed by Rooney *et al.*[8]; our result is very similar to theirs. Therefore, the radical shown in Fig. 7 seems to be a cationic radical produced from *p*-xylene. There is a possibility that the spectra of ArH–Cu–$AlCl_3$ obtained are formed merely by an interaction of aromatic compounds with aluminium chloride. However, this can be excluded on the basis of the following facts: (1) Both the colour and the ESR spectra of ArH–Cu–$AlCl_3$ are different from those of the aromatic compound–$AlCl_3$ systems. (2) The copper(I) ion does not produce any radical species under a vacuum even in the presence of aluminium chloride. Therefore, the cationic radicals in ArH–Cu–$AlCl_3$ are essentially different from those in aromatic compound–$AlCl_3$ systems.

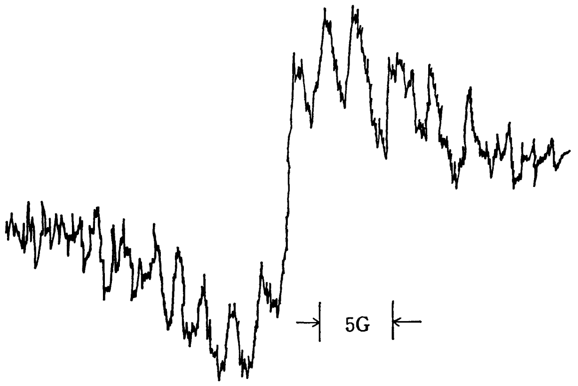

Fig. 7. ESR spectrum of *p*-xylene–$AlCl_3$.

Summary. From the results obtained so far, it can be concluded that a transfer of an electron from the benzene ring to Cu(II)–$AlCl_3$ occurs and that a cationic radical is formed. In this process, the copper(II) ion is reduced to the copper(I) state. The cationic radical thus formed is stabilized by an interaction with Cu(I)–$AlCl_3$:

$$\text{ArH} + \text{Cu(II)} + \text{AlCl}_3 \longrightarrow \text{ArH}^{+}\cdots\text{Cu(I)}\cdots\text{AlCl}_3$$

However, it is not yet known whether the cationic radical is in a monomer or a dimerized form.

The copper(I) ion produces no cationic radical, although it reacts readily with aluminium chloride and aromatic compounds. On the addition of oxygen to the system, the copper(I) ion is oxidized to the copper(II) ion, which removes a π-electron from the benzene ring and produces the cationic radical:

$$\text{ArH} + \text{Cu(I)} + \text{AlCl}_3 \longrightarrow \text{ArH}\cdots\text{Cu(I)}\cdots\text{AlCl}_3 \xrightarrow{O_2}$$
$$[\text{ArH}\cdots\text{Cu(II)}\cdots\text{AlCl}_3] \longrightarrow \text{ArH}^{+}\cdots\text{Cu(I)}\cdots\text{AlCl}_3$$

A complete assignment of the hfs of the spectra could not be achieved; a detailed investigation is, therefore, now under way using the ENDOR technique.

References

1) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).

2) Y. Takegami, Y. Watanabe, and T. Suzuki, Jpn Pat. 28977 (1972).

3) This residual solid material was decomposed by adding tetrahydrofuran, and the *p*-xylene content was determined roughly as 23 wt% by the use of a gas chromatograph.

4) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

5) R. E. V. Dyke, *J. Am. Chem. Soc.*, **72**, 3619 (1950).

6) H. C. Brown and W. J. Walace, *J. Am. Chem. Soc.*, **75**, 6265 (1953); **75**, 6268 (1953).

7) S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 903 (1966).

8) J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.* (*London*), **1961**, 142.