CHEMISTRY LETTERS, pp. 201-204, 1986.

INTERACTION BETWEEN ALUMINIUM COPPER(I) CHLORIDE AND 1,3-DIPHENYLPROPANE

Hidefumi HIRAI,* Keiichi KANAKA, and Makoto KOMIYAMA
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Tokyo 113

A strong charge-transfer band due to the interaction between aluminium copper(I) chloride and 1,3-diphenylpropane is observed in the 360-500 nm region. The band, which is composed of two portions with absorption maxima, respectively, at 422 and 460 nm, is attributed to chelate-type interactions of the two aromatic rings of 1,3-diphenylpropane with aluminium copper(I) chloride.

Aluminium copper(I) chloride ($AlCuCl_4$), a double metal salt composed of copper(I) chloride and aluminium chloride, interacts with various aromatic compounds such as benzene, toluene, and mesitylene in solutions.[1)] The X-ray analysis [2)] on the crystal of the $AlCuCl_4$-benzene complex showed 1:1 interaction between benzene and copper(I) ion in $AlCuCl_4$.

Previously, the authors showed that 1,3-diphenylpropane solutions of $AlCuCl_4$ [3)] and toluene solutions of $AlCuCl_4$ containing polystyrene [4-6)] were water-resistant absorbents of carbon monoxide. The water-resistivities were attributed to protection of $AlCuCl_4$ by 1,3-diphenylpropane or by polystyrene, since toluene solutions of the double metal salt without 1,3-diphenylpropane or polystyrene were rapidly deactivated by water vapor due to irreversible reaction.

This paper reports the results of electronic absorption spectroscopy on various aromatic solutions of $AlCuCl_4$. It is shown that interaction of 1,3-diphenylpropane with $AlCuCl_4$ is entirely different from interactions of mono-aromatic ring compounds such as benzene and toluene with the double metal salt.

1,3-Diphenylpropane was prepared from 1,3-diphenylpropan-2-one and hydrazine.[7)] Benzene and toluene were distilled after being dried over metallic sodium. Copper(I) chloride was reprecipitated from aqueous hydrochloric acid solution by addition of water, and was dried in vacuo at 80 °C for 24 h. Aluminium chloride was purified by sublimation.

Aromatic solutions of $AlCuCl_4$ were prepared by incubating copper(I) chloride and aluminium chloride in the corresponding aromatic solvents at 40 °C for 4 h under dry nitrogen. The charged molar ratio of copper(I) chloride to aluminium chloride was kept at 1.1. Then, the supernatant was put into a 1 mm quartz cell with shielding cap under dry nitrogen. Absorption spectra were measured on a Hitachi model 340 spectrometer at 25 °C.

The line (1) in Fig. 1 shows the absorption spectrum of 1,3-diphenylpropane solution of $AlCuCl_4$. A strong charge-transfer band is observed in the 360-500 nm region. The band has an absorption maximum at 460 nm and is composed of multiple components.

A curve resolving study showed that the observed charge-transfer band was satisfactorily expressed by the sum of the two bands depicted by the dashed lines in Fig. 1. Absorption maxima of these two resolved bands, respectively, were located at 422 and 460 nm, and half band widths were 87 and 44 nm. The resolution was carried out under the assumption of Gaussian band shape, using peak position, peak height, and half band width as variable parameters.

In contrast to the strong charge-transfer band for the 1,3-diphenylpropane solution of $AlCuCl_4$, benzene or toluene solution of the double metal salt exhibits only quite a weak absorption band at 370-380 nm as shown by the lines (2) and (3) in Fig. 1. No absorption band is detected at a longer wavelength than 400 nm. Thus, the interactions of mono-aromatic ring compounds such as benzene and toluene with $AlCuCl_4$ are entirely different from that of 1,3-diphenylpropane with the double metal salt. The appearance of strong charge-transfer band in the 1,3-diphenylpropane-$AlCuCl_4$ system is definitely attributable to the presence of two aromatic rings in one molecule of 1,3-diphenylpropane. The two aromatic rings of 1,3-diphenylpropane interact with one $AlCuCl_4$ molecule, and the interactions mutually enhance each other due to chelate-effect.

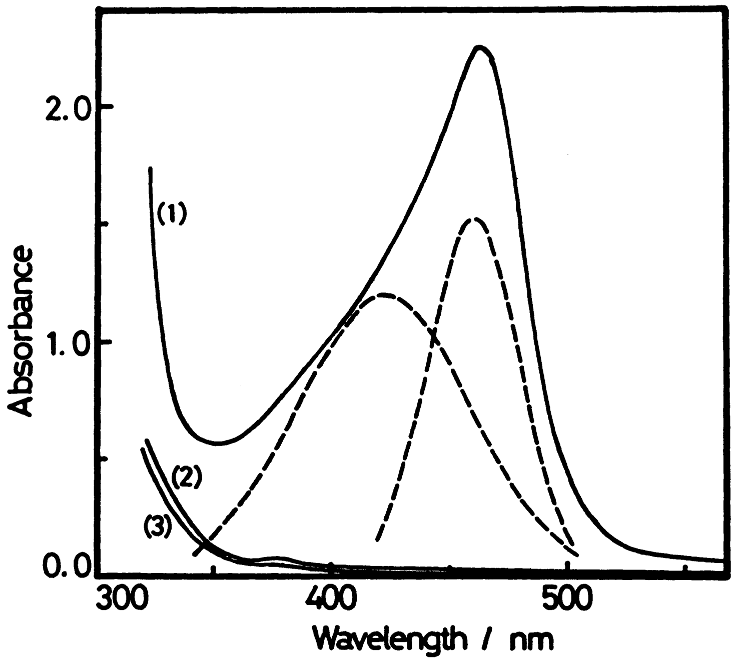

Fig. 1. Electronic absorption spectra of $AlCuCl_4$ in 1,3-diphenylpropane (1), toluene (2), and benzene (3) at 25 °C under nitrogen: $[AlCuCl_4]_0$ = 0.63 mol dm^{-3} ; the dashed lines show the resolved absorption bands for the spectrum (line (1)) of the 1,3-diphenylpropane solution of $AlCuCl_4$; cell length, 1 mm; the suffix 0 refers to the charged concentration.

Figure 2 shows the absorption spectra for benzene solutions of 1,3-diphenylpropane and $AlCuCl_4$. Here the concentration of 1,3-diphenylpropane is changed from 2.50 to 0.16 mol dm^{-3}, keeping the concentration of $AlCuCl_4$ constant at 0.63 mol dm^{-3}. Benzene solutions of $AlCuCl_4$ without 1,3-diphenylpropane exhibit only weak charge-transfer bands at 370-380 nm, as depicted by the line (3) in Fig. 1. As the concentration of 1,3-diphenylpropane decreases (from line (1) to line (4)), the charge-transfer band gradually broadens and the apparent absorption maximum shifts towards shorter wavelength. These results indicate that there are two types of chelate interactions in the 1,3-diphenylpropane-$AlCuCl_4$ system, and that the contribution of each of the interactions varies with changing concentration of 1,3-diphenylpropane.

According to a curve resolving study, all the four spectra in Fig. 2 are composites of two overlapping bands with absorption maxima, respectively, at 422 and 460 nm, and with half band widths of 87 and 44 nm. All of these values are identical with those of the two resolved bands obtained for the spectrum of the 1,3-diphenylpropane-$AlCuCl_4$ system in Fig. 1. The relative intensities of the band at 460 nm at the concentrations 1.25, 0.32, and 0.16 mol dm^{-3} of 1,3-diphenylpropane, with respect to the value at the concentration 2.50 mol dm^{-3}, are 0.5, 0.4, and 0.1, respectively. The corresponding relative intensities of the band at 422 nm, with respect to the intensity of the band at the concentration 2.50 mol dm^{-3}, are 1.1, 0.7, and 0.3, respectively. Thus, the contribution of the band at 460 nm decreases with decreasing concentration of 1,3-diphenylpropane more

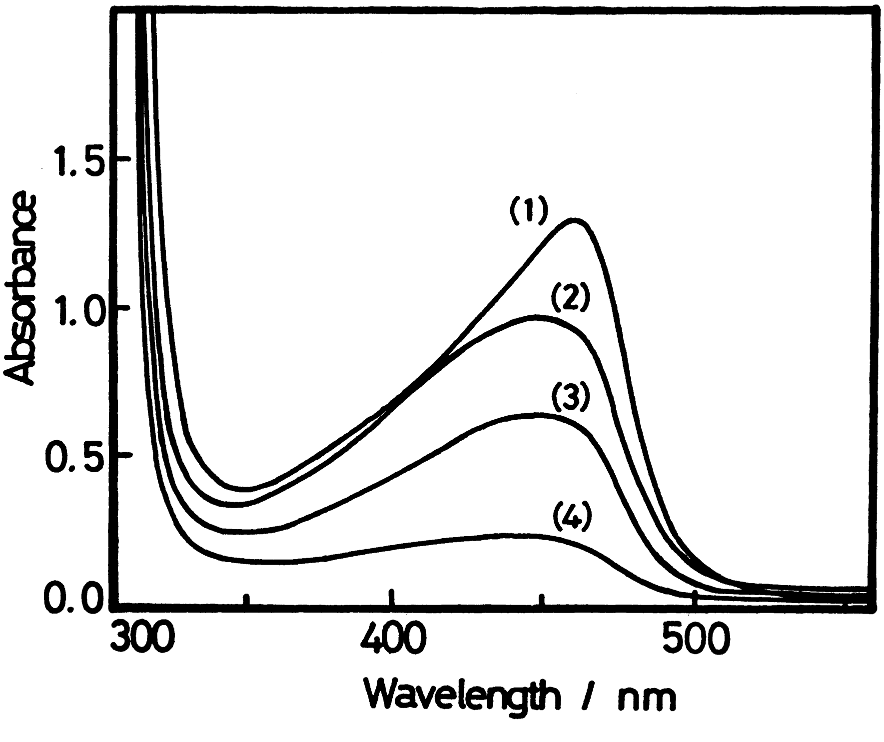

Fig. 2. Electronic absorption spectra of benzene solutions of $AlCuCl_4$ containing 1,3-diphenylpropane in various concentrations: $[1,3\text{-diphenylpropane}]_0$ = 2.50 (1), 1.25 (2), 0.32 (3), and 0.16 mol dm^{-3} (4); $[AlCuCl_4]_0$ = 0.63 mol dm^{-3} ; cell length, 1 mm.

drastically than that of the band at 422 nm. This result shows that the chelate interaction between 1,3-diphenylpropane and $AlCuCl_4$, which is responsible for the band at 460 nm, is energetically less stable than the one responsible for the band at 422 nm. A possibility that both of the two absorption bands at 422 and 460 nm originate from only one chelate interaction is definitely ruled out.

Two types of chelate interactions between 1,3-diphenylpropane and $AlCuCl_4$ are proposed as follows. In one of them, an aromatic ring of 1,3-diphenylpropane interacts with the copper(I) part of $AlCuCl_4$ and another aromatic ring interacts with a chlorine atom of the aluminium chloride moiety in the same $AlCuCl_4$ molecule. In the second chelate interaction, both of the two aromatic rings can interact with each of the two chlorine atoms of the aluminium chloride portion. The interaction between the aromatic ring and the copper(I) ion gives rise to the absorption band at 422 nm, and the one between the aromatic ring and the chlorine atom of the aluminium chloride portion yields the band at 460 nm. These arguments, which are based on the assumption that the interaction of the aromatic ring with the copper(I) ion is stronger than that with the chlorine atom, are consistent with the results of X-ray crystallography 2) and ^{13}C-NMR spectroscopy 8) showing interactions of aromatic rings of mono-aromatic compounds with the copper(I) ion in $AlCuCl_4$.

In conclusion, a strong charge-transfer band due to the interaction between 1,3-diphenylpropane and aluminium copper(I) chloride is observed. The strong absorption band is attributed to chelate-type interactions of the two aromatic rings of a 1,3-diphenylpropane molecule with an aluminium copper(I) chloride molecule.

A quantitative study on the interaction is currently under way.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

References

1) H. Hirai, M. Nakamura, and M. Komiyama, Bull. Chem. Soc. Jpn., 56, 2519 (1983).
2) R. W. Turner and E. L. Amma, J. Am. Chem. Soc., 88, 1877 (1966).
3) H. Hirai, S. Hara, and M. Komiyama, Chem. Lett., 1984, 861.
4) H. Hirai, M. Komiyama, and S. Hara, Makromol. Chem., Rapid Commun., 2, 495 (1981).
5) H. Hirai, M. Komiyama, and S. Hara, Chem. Lett., 1981, 1443.
6) H. Hirai, S. Hara, and M. Komiyama, Bull. Chem. Soc. Jpn., 59, 109 (1986).
7) D. J. Cram and H. Steinberg, J. Am. Chem. Soc., 73, 5691 (1951).
8) H. Hirai, K. Kanaka, and M. Komiyama, 50th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1985, Abstr., No. 1L06.

(Received November 13, 1985)