Interaction between Aromatics and Zinc Chloride. II. The Formation of σ-Complexes and Cation Radicals on Supported Zinc Chloride

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Synopsis. Anhydrous zinc chloride supported in the solid state was found to produce colored intermediates by reactions with aromatics (anthracene, naphthacene, pentacene, pyrene, pelyrene, and chrysene) at 60 °C. The measurements of their electronic absorption spectra and ESR spectra confirmed that these were the same aromatics–zinc chloride σ-complexes and aromatics cation radicals as those formed in molten zinc chloride.

It has been known that Lewis acids, such as boron trifluoride[1)] and aluminum chloride,[2)] react with aromatic hydrocarbons to form σ-complexes (electron donor–acceptor (EDA) complexes) and aromatics cation radicals. Our previous work revealed that molten zinc chloride also produced similar intermediates by means of reactions with aromatic hydrocarbons at higher temperatures.[3)]

In order to advance further studies of the catalytic behavior of zinc chloride, we wish to confirm the reactivity of the aromatics–zinc chloride system with anhydrous zinc chloride supported on a porous Vycor glass at lower temperatures. Its high surface area and good transmission of light enabled us to measure better the electronic and ESR spectra.

The electronic absorption spectra of aromatics–zinc chloride colored complexes produced on the zinc chloride supported in the solid state were essentially similar to those of molten zinc chloride[3)] and of aluminum chloride in the solid state.[2)] Furthermore, the ESR signals were detected for the colored complexes. Based on these results, it was concluded that the zinc chloride supported in the solid state reacted directly with aromatic hydrocarbons to form the σ-complexes (EDA-complexes) and the cation radicals.

Experimental

Materials. The anthracene, naphthacene, pentacene, pyrene, perylene, chrysene, zinc metal, and silver chloride were all purchased and were all of a G. R. grade; they were used without further purification.

The rod of porous Vycor glass(Corning No. 7930) used as a support was ground to 100 mesh. The powdered Vycor glass was treated with a concd HNO_3 solution at room temperature overnight and washed with distilled water to remove foreign metal ions as impurities. Having been dried at 140 °C, it was heated in air at 600 °C for 6 h to burn off the organic contaminants. Its surface area was 154 m^2/g.

Preparation of Supported Zinc Chloride. Anhydrous zinc chloride was prepared by the reaction of zinc metal with siliver chloride at about 500 °C in a vacuum at 10^{-3} Torr and vaporized so as to be supported on the purified Vycor glass preliminarily heated at 500 °C for 4 h in a vacuum. The anhydrous zinc chloride content was 5—10 wt% in the present support.

Reaction. About 500 mg of the supported zinc chloride was transferred into a 1-mm-thick quartz cell in a vacuum and thoroughly mixed with 5 mg of an aromatic compound in the cell. After the cell had then been evacuated below 10^{-3} Torr, its neck was fused so as to seal it off. Then the cell was heated at a constant temperature above 60 °C. The formation of a colored product could be observed on the supported zinc chloride.

Electronic Spectra and ESR Signals. The electronic spectra of the colored products were measured at room temperature with a Hitachi 624 spectrometer equipped with an integrating sphere. The ESR signals were detected also at room temperature with a JES-ME-3X spectrometer for samples prepared in ESR tubes by a way similar to that described above.

Results and Discussion

The rate of the formation of aromatics–zinc chloride complexes was found to be depend on the aromatic hydrocarbon source. Under the present conditions, aromatic compounds with higher ionization potentials, such as benzene, naphthalene, and phenanthrene, could not be observed to form colored products. At higher temperatures and longer contact times, the transmittance of the samples gradually decreased and the characteristic absorption spectra of the complexes became obscure because of the formation of other compounds, such as condensed products of aromatics.

Figure 1 shows the absorption spectra of the colored products on the supported zinc chloride for anthracene, naphthacene, pentacene, pyrene, perylene, and chrysene; the positions of these absorption bands are summarized in Table 1 for comparison. These absorp-

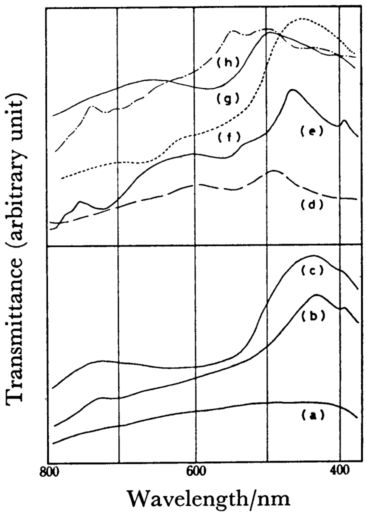


Fig. 1. Electronic absorption spectra of aromatics–$ZnCl_2$ complexes.
(a): Original, (b) and (c): anthracene at 60 °C for 10 min and for 120 min, (d): naphthacene, (e): pentacene, (f): chrysene, (g): pyrene, (h): perylene, each at 100 °C for 30 min.

TABLE 1. COMPARISON OF THE ABSORPTION BANDS OF σ-COMPLEXES AND RADICALS IN SUPPORTED ZINC CHLORIDE WITH THOSE IN THE MOLTEN ZINC CHLORIDE, ALUMINUM CHLORIDE, AND Na–THF SYSTEMS

Specie	Systems[a)]	Anthracene	Naphthacene	Pentacene	Pyrene	Perylene	Chrysene
σ-Complex	A	430	470	493	495	505	455
	B	425	460				
	C	420	468	440	481	637	
Radicals, or ions	A	730	395, 755, 775			545, 635, 735	690
	B	725	710				
	C	735	395, 670, 769				
	D	366, 705	398, 793	431, 847	492, 719	581, 675, 724	

(unit; nm)

a) A: zinc chloride supported on a porous Vycor glass, B: molten zinc chloride,[3)] C: aluminum chloride in the solid state,[2)] D: Na–THF.[5,6)]

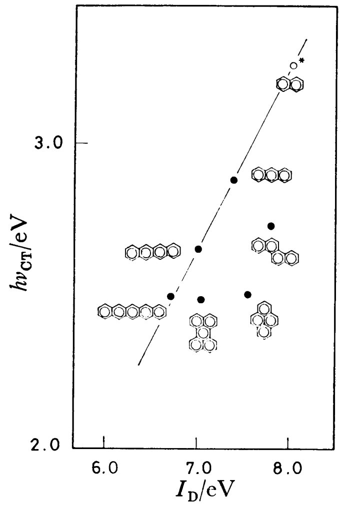
tion bands disappeared when the colored products were placed in contact with water vapor.

The supported zinc chloride itself did not give any absorption band within the entire wavelength region measured in this work. When anthracene came in contact with the supported zinc chloride at 60 °C, a broad absorption band at 430 nm appeared at first, and then another absorption band developed at 730 nm after prolonged contact time. Similarly, in the reaction with the supported zinc chloride at 100 °C for 30 min, naphthacene gave three weak and sharp absorption bands at 395, 755, and 775 nm, in addition to a strong, broad absorption band at 470 nm and a broad absorption band at 650 nm. Pentacene gave two broad absorption bands at 493 and 590 nm; pyrene gave two broad absorption bands at 495 nm and 650 nm; perylene gave a strong absorption band at 505 nm, a strong sharp absorption band at 545 nm and two weak absorption bands at 635 and 735 nm, and chrysene gave two absorption bands at 455 and 690 nm.

σ- or EDA-Complex Formation. As may be seen in Table 1, the absorption bands observed at 430 nm for anthracene, at 470 nm for naphthacene, at 493 nm for pentacene, and at 495 nm for pyrene on the supported zinc chloride were found to be almost the same as those at 420 nm, at 468 nm, at 440 nm, and at 481 nm respectively of the corresponding aromatics–aluminum chloride complexes in the solid state.[2)] Furthermore, the absorption bands seen at 430 nm for anthracene and at 470 nm for naphthacene were consistent with those at 425 nm and at 460 nm of the corresponding aromatics–molten zinc chloride complexes.[3)] The colored complexes on solid aluminum chloride or in molten zinc chloride are assigned to the σ-complexes (π, v-, or EDA-complexes), and the characteristic absorption bands, to the charge-transfer ones.[2,3)]

Figure 2 shows the linear correlation between the characteristic absorption energy of the present complexes, $h\nu_{CT}$, and the ionization potential, I_D, of the corresponding aromatics; although the absorption energy of the pyrene- and chrysene-zinc chloride complexes and the slope of the line deviate somewhat from the law of the charge-transfer complexes,[4)] these aromatics–zinc chloride complexes seem to be EDA-complexes, *i.e.*, σ-complexes (*cf.* Ref. 3).

Ion or Radical Formation. When the colored complexes on the supported zinc chloride were treated at higher temperatures, the spectra changed to those characteristic to cation radicals. Except for perylene, all the present samples also gave a broad singlet paramagnetic signal whose *g*-value was about 2.0036 for anthracene, 2.0037 for naphthacene, 2.0031 for pentacene, 2.0031 for pyrene, and 2.0032 for chrysene. The perylene on the supported zinc chloride gave the same ESR spectrum, split into seven signals with equal hyperfine splitting (0.3 mT), as was detected on silica–alumina.[7)] The *g*-value was about 2.0038.



* Cited from Ref. 3.

Fig. 2. Relation between the position of CT bands and ionization potentials of donors.

These findings support the idea that aromatics–cation radicals can be formed in the aromatics–supported zinc chloride system, where the radical cations are supposedly produced by the ionization of the σ- or EDA-complexes.

The assignment of the electronic spectra for cation radicals of the aromatics is well established.[3,5,6)] The positions of the bands are also summarized in Table 1.

Anthracene in molten zinc chloride gave another electronic absorption band at 620 nm;[3)] this band is attributed to the dipositive ion[5,7)] or to a secondary σ- or π-complex produced by anthracene and the anthracene–zinc chloride σ-complex.[8)] This band did not appear in the anthracene–supported zinc chloride system; therefore, such intermediates cannot be considered for the supported zinc chloride under the present conditions.

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