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Interaction between Aromatics and Zinc Chloride in the Molten State. The Formation of σ-Complexes and Radicals

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The electronic absorption spectra of naphthalene, anthracene, and naphthacene in dried, molten zinc chloride were measured and found to be almost the same as those of aromatics–aluminum chloride complexes in the solid state. ESR measurements were also made; they confirmed the presence of radicals. From these results, it was concluded that the aromatics reacted with molten zinc chloride to form EDA-complexes, *i. e.*, σ-complexes and cation radicals.

It has been known that a massive quantity of zinc chloride used in the molten state is a superior catalyst for the hydrocracking of polycondensed aromatics into gasoline fractions, although partial hydrogenation is predominant when the amount of zinc chloride is relatively small; the activity of the catalyst has been considered to originate in a proton produced by the dissociation of water coordinated to the zinc chloride molecule.[1–4]

However, when aromatics come into contact with dried, molten zinc chloride under a vacuum, colored products are observed to be produced. This suggests that the products are complexes of the electron donor-acceptor type and might also play a role in the hydrocracking of aromatics as reaction intermediates, because we have already confirmed that, in the hydrocracking of aromatics with molten zinc chloride, the conversion is correlated with their ionization potentials.[2]

The measured electronic spectra of aromatics–zinc chloride complexes were almost the same as those of aromatics–aluminum chloride complexes in the solid state observed by Perkampus and Kranz[5] and by Sato and Aoyama.[6] Furthermore, the complexes gave strong ESR signals of the singlet type.

From these results, aromatics and zinc chloride in the molten state were found to form σ-complexes, radicals, and additional intermediates between the σ-complexes and the aromatics.

Experimental

Materials. Zinc chloride, naphthalene, anthracene, and naphthacene of the G. R. grade were used without purification.

Electronic Absorption Spectra. Zinc chloride, after having been introduced into the rectangular quartz cell shown in Fig. 1, was heated at 200±10 °C under a vacuum below 10^{-3} Torr in an electric furnace for 2—3 h. After the cell has then cooled to room temperature, an aromatic compound sample in a vacuum stopcock (*cf.* Fig. 1) was dropped into the cell. The cell was then evacuated again at about 10^{-3} Torr, and the upper neck of the cell was sealed off by fusion. The cell containing the sample was then heated in an electric furnace above 280 °C to melt it. When this molten zinc chloride was placed in sufficient contact with aromatics, colored products were observed to develop in the transparent molten zinc chloride. This sample cell was mounted in a specially constructed cell holder kept at 300±10 °C, and the absorption spectra were measured with a Hitachi 624-type spectrophotometer.

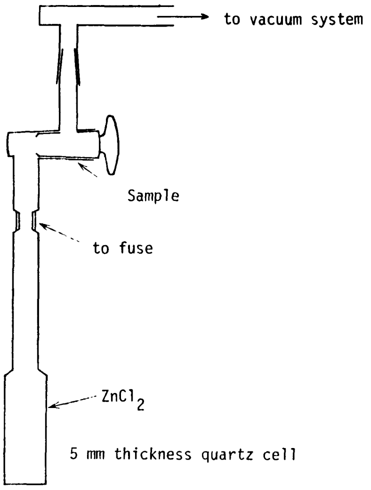


Fig. 1. Apparatus for the absorption spectroscopic study.

To confirm more exactly the formation of colored products of the σ-type, anhydrous zinc chloride was carefully prepared from silver chloride and metallic zinc powder in a vacuum according to a procedure similar to Wallace and Willard's for the preparation of anhydrous aluminum chloride;[7] it was then reacted with anthracene in a sealed glass tube.

ESR. Samples for the ESR measurements were prepared in ESR tubes in a way similar to that described above. The ESR signals were measured with a Jasco model ME-type spectrometer at room temperature, while the g-values were determined by the use of MnO as the reference substance.

Results and Discussion

Electronic Absorption Spectra. The absorption spectra of the colored products in molten zinc chloride for naphthalene, anthracene, and naphthacene are shown in Fig. 2 and are summarized in Table 1 for purposes of comparison.

The spectrum of molten zinc chloride only (Fig. 2-(1)) did not show any special absorption bands within the range in question. Upon reaction with molten zinc chloride, anthracene gave three absorption bands at 425, 620, and 725 nm (Fig. 2-(3)), naphthalene gave two weak absorption bands at 385 and 590 nm (Fig. 2-(2)), and naphthacene gave strong absorption bands at 360 and 460 nm (Fig. 2-(4)). After prolonged contact, a new band at 705 nm for naphthalene (Fig. 2-(2′)) and one at 710 nm for naphthacene (Fig. 2-(4′))

TABLE 1. COMPARISON OF THE ABSORPTION BANDS OF THE σ-COMPLEXES, RADICALS, HF-BF$_3$, BF-1,2-DICHLOROETHANE, AND Na- OR K-THF SYSTEMS

Species	System	Naphthalene	Anthracene	Naphthacene
σ-Complex	A	385	425	460
	B	380	420	468
	D		423	452
Proton-addition complex	C	390	408	435
Radical, monopositive ion, or negative ion	A	705	725	710
	B		735	355, 385, 395, 670, 769, 850
	E	366, 735, 813	369, 715	359, 403, 704
Dinegative ion or others	A	590	620	360
	B		665	
	E		333, 613	353, 398, 621
			(unit; nm)	

A; Molten zinc chloride. B; Aluminum chloride.[5,6] C; HF-BF$_3$.[10,11] D; BF$_3$-1,2-Dichloroethane.[9] E; Sodium- or Potassium-THF.[16,17]

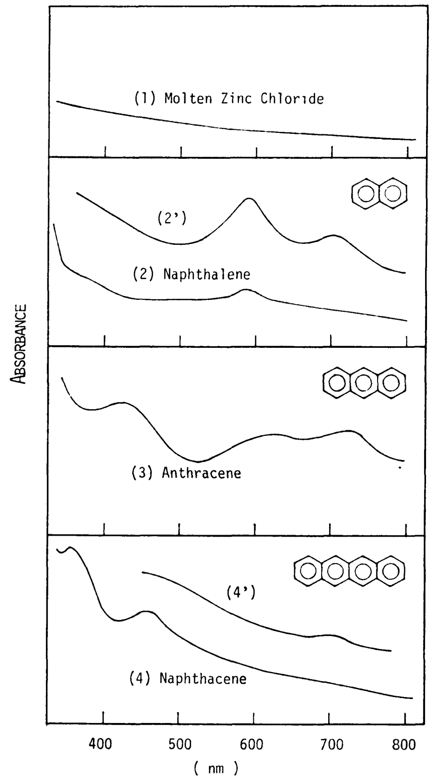


Fig. 2. Absorption spectra of aromatics in molten zinc chloride. Absorbance *vs.* wavelength (nm).
(1) Molten zinc chloride, (2)(2′) naphthalene, (3) anthracene, (4)(4′) naphthacene.

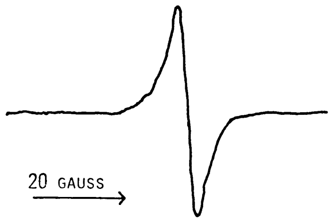


Fig. 3. ESR spectrum of naphthalene cation radical formed in molten zinc chloride.

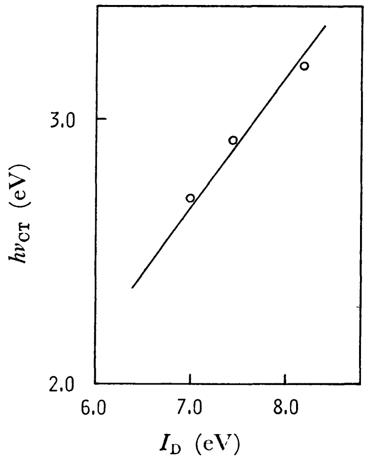


Fig. 4. Dependence of the position of CT bands on ionization potentials of donors.

were observed to develop.

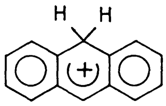
ESR Signals. All the samples gave strong and broad singlets with the *g*-values of 2.0028, 2.0031, and 2.0030 for naphthalene, anthracene, and naphthacene respectively (*cf.* Fig. 3).

σ-Complex Formation. As may be seen in Table 1, the absorption bands at 385 nm for naphthalene, 425 nm for anthracene, and 460 nm for naphthacene in molten zinc chloride were found to be almost the same as those of the corresponding aromatics–aluminum chloride complexes in the solid state, the latter being confirmed as σ-complexes(π, v-complexes according to their notation) by Perkampus and Kranz.[5]

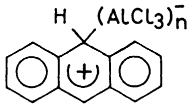
Figure 4 shows the linear correlation between their absorption energy, $h\nu_{CT}$, and the ionization potential, I_D, of the corresponding aromatics; this correlation suggests EDA-complex, *i.e.*, σ-complex formation, as in the case of aromatics–ethanol–zinc chloride–chloroform system investigated previously by the present authors.[8]

However, since the proton-addition complexes are quite similar to the σ-complexes in the position of the absorption band (Table 1),[9-11] we tried to eliminate the effect of the trace amount of water on the complex formation in the present system; it could be confirmed that a colored product was produced by the reaction of anthracene with anhydrous molten zinc chloride carefully prepared from zinc metal and silver chloride in a vacuum.

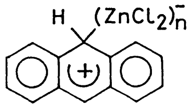
These results strongly suggest that aromatics directly react with molten zinc chloride to form EDA-complexes, *i.e.*, σ-complexes. Accordingly, the absorption bands at 385 nm for naphthalene, 425 nm for anthracene, and 460 nm for naphthacene can be attributed to the formation of aromatics–zinc chloride σ-complexes.



(A)



(B)



(C)

The structure of the proton-addition complexes of aromatics proposed by Gold and Tye[12] has been both experimentally and theoretically confirmed;[11,13,14] for example, the proton-addition complex of anthracene has been fomulated in the form of (A). Perkampus and Kranz proposed the (B) structure for the anthracene–aluminum chloride complex on the basis of the similarity in the absorption spectrum.[5] The (C) structure can also be proposed for the anthracene–zinc chloride complex on the basis of the similarity of the absorption spectrum of anthracene in molten zinc chloride with that in aluminum chloride in the solid state.

Ion or Radical Formation. Naphthalene in molten zinc chloride has a paramagnetic property and a characteristic color which gradually changes from purple to dark green.[15] It gave an absorption band at 705 nm quite different from the absorption band for sodium[16] or potassium[17] naphthalenide in the THF solution assigned as a free radical. However, this band is assumed to correspond to the naphthalene cation radical, because it is more difficult for naphthalene to form a radical than for the other two aromatics and because the band at 705 nm in the spectrum of Fig. 2-(2′) and the strong ESR signal appeared only when naphthalene was in sufficient contact with molten zinc chloride. The band at 590 nm in the spectrum of Fig. 2-(2) or (2′) has been attributed to the dipositive ion or an intermediate between naphthalene and the naphthalene–zinc chloride σ-complex, as Sato predicted,[6] but further investigation is necessary for a certain assignment.

Distler and Hohlneicher showed that the anthracene cation radical has absorption maximum at 735 nm, and the naphthacene radical, at 348, 397, 667, 752, and 833 nm.[18] The present work confirmed that anthracene, when in sufficient contact with molten zinc chloride, showed a characteristic deep green color[15] and was strongly paramagnetic. The absorption band at 725 nm can thus be attributed to the formation of the cation radical derived by the ionization of the σ-complex (C). The absorption band at 620 nm seemed to correspond to that observed on the silica-alumina surface[19] and that observed for the anthracene–aluminum chloride complex.[6] Hall[19] supposed that the 665 nm species might be a dipositive anthranium ion on the basis of Aalbersbers's work[20] and from the calculations of Balk *et al.*[21] Sato and Aoyama proposed that it might be a secondary σ- or π-complex produced by anthracene and the anthracene–aluminum chloride σ-complex. In the case of the anthracene–molten zinc chloride system, further investigation is necessary to assign the band at 620 nm.

In the case of naphthacene, the formation of the cation radical was also confirmed by the production of ESR signals and the characteristic blue color.[15] The absorption spectrum (Fig. 2-(4)) did not show any special band within the range between 500 and 800 nm, but a weak absorption band around 710 nm (Fig. 2-(4′)) grew with prolonged contact. This band may be attributed to one band of the naphthacene cation radical. The absorption band about 360 nm may be supposed to be overlapped with the absorption bands of naphthacene itself, the cation radical, and the dipositive ion.

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