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Interaction between Aromatics and Zinc Chloride. III. The Dissociation of Triphenylmethane and 9,10-Dihydroanthracene into Ions

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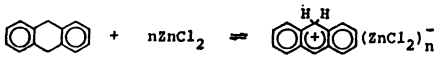
Triphenylmethane and 9,10-dihydroanthracene were found to produce colored complexes when placed in contact with molten zinc chloride or with solid zinc chloride pulverized or supported on porous Vycor glass. The triphenylmethane complex gave the same electronic absorption spectrum as that of the triphenylmethyl cation generated by contact with silica–alumina and BF_3 on silica. The 9,10-dihydroanthracene complex exhibited the same electronic absorption band as that of the 9-anthracenium ion produced by the reaction of anthracene with concd H_2SO_4. The reaction of the triphenylmethane complex with deuterium gas provided HD gas and $(C_6H_5)_3CD$. Similarly, the 9,10-dihydroanthracene complex and deuterium gas produced HD gas and 9,10-dihydroanthracene-9-*d*. Furthermore, their colored complexes on the supported zinc chloride gave a very weak IR absorption band at about 1720 cm^{-1}, which is interpreted as corresponding to the formation of a Zn–H bond. These observations led us to conclude that triphenylmethane and 9,10-dihydroanthracene dissociate into ions upon contact with zinc chloride:

$$(C_6H_5)_3CH + n\mathrm{ZnCl}_2 \rightleftarrows (C_6H_5)_3C^+(\mathrm{ZnCl}_2)_n^-H$$



As has previously been reported,[1,2] zinc chloride reacts with aromatic hydrocarbons to form $(\mathrm{Ar}^+)(\mathrm{ZnCl}_2)_n^-$ electron-donor acceptor-complexes(Ar: aromatics). It has been suggested that these$(\mathrm{Ar}^+)(\mathrm{ZnCl}_2)_n^-$ EDA-complexes act as reaction intermediates in the hydrogenation and hydrocracking of aromatic hydrocarbons over a zinc chloride catalyst; their conversions are correlated positively to the ionization potentials of the corresponding aromatic hydrocarbons.[3]

As a part of a systematic study to elucidate the behavior of the zinc chloride catalyst in the hydrocracking of aromatic hydrocarbons, which would be helpful for this reaction,[4,5] the mechanism of the ionization of triphenylmethane and 9,10-dihydroanthracene was investigated by measurements of the electronic and IR absorption spectra of the colored complexes formed in molten zinc chloride or on solid zinc chloride, which was powdered or supported on porous Vycor glass, by means of exchange reactions with deuterium gas and by the analyses of their reaction products.

Experimental

Materials. Triphenylmethane and 9,10-dihydroanthracene of a G. R. grade were used without further purification. Porous Vycor glass plate and powder were used as supports of the zinc chloride for measuring the IR and electronic absorption spectra. The other chemicals were the same as those mentioned in our previous work.[2]

Apparatus and Procedure. Anhydrous zinc chloride was prepared and attached onto a porous Vycor glass support as described in the previous paper.[2] Triphenylmethane or 9,10-dihydroanthracene was allowed to react with zinc chloride under various conditions, and changes in the transmittance or in the reflectance of visible light by the colored complexes were measured with a Hitachi 624 spectrophotometer equipped with an integrating sphere.

For the measurements of the IR absorption spectra, a cell device designed by Angel *et al.*[6] and Hino[7] was used. A rod of porous Vycor glass was sliced into a plate with 0.3 mm thick, and then it was cut to fit the cell windows. After zinc chloride and a plate purified by the method described previously[2] has been introduced into the cell device, the device was evacuated to below 10^{-4} Torr at about 500 °C until 10—20 wt % of the zinc chloride had evaporated onto the plate. The cell was then cooled to room temperature, and a hydrocarbon was introduced from the top of the cell under a vacuum and brought to full contact with the supported zinc chloride at the reaction temperature until colored products formed on the catalyst. The IR absorption spectra were measured with a JASCO IRA-2 spectrophotometer.

For the D_2-exchange reaction, a glass vessel 17 ml in size was used as a reactor. About 3 g of dehydrated zinc chloride or 500 mg of supported zinc chloride and about 5 mg of a reactant were charged into the vessel under a vacuum, and then deuterium gas was introduced at 600 Torr. The vessel was heated at a given temperature for a given time.

Analysis. After the measurements of the electronic absorption spectra of the colored products, water was introduced into the quartz cell and the mixture was extracted with a large amount of tetrahydrofuran and dichloromethane. The extracts were analyzed by gas chromatography. The details were described in a previous paper.[8]

The D_2-exchanged products were identified by the use of a Finnigan 3000 mass spectrometer. The formation of HD gas was confirmed by the method reported by Sato *et al.*[9]

Results and Discussion

Electronic Absorption Spectra. Triphenylmethane produced a colored complex upon contact with dehydrated solid zinc chloride, anhydrous zinc chloride supported on porous Vycor glass, and porous Vycor glass alone pretreated at 550 °C. The complex exhibited a characteristic double-peaked absorption band in the 415—450 nm region of the spectrum, as is shown in Figs. 1(a)—(d). The (a) spectrum was obtained by measuring the reflectance of the triphenylmethane

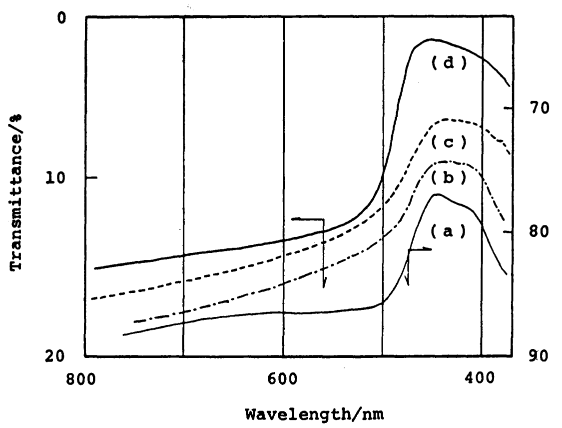


Fig. 1. Electronic spectra of triphenylmethane on zinc chloride, supported zinc chloride, and a support.
(a): On solid zinc chloride which was dehydrated by melting under a vacuum, at room temperature for 7d, (b): on powdered zinc chloride which was dehydrated at 250 °C for 3 h under a vacuum, at 220 °C for 10 min, (c): on porous Vycor glass pretreated at 550°C, at 70°C for 180 min, (d): on anhydrous zinc chloride supported on porous Vycor glass, at room temperature for 20 h.

yellow intermediate formed on the solid zinc chloride dehydrated by melting under a vacuum in a quartz cell. The spectra from (b) to (d) were measured for the transmittance of the yellow complex developed on the powdered zinc chloride, the pulverized porous Vycor glass, and the supported zinc chloride. This double-peaked absorption band disappeared when the complex was treated with water vapor.

9,10-Dihydroanthracene also gave a yellow intermediate upon contact with anhydrous zinc chloride supported on porous Vycor glass or with molten zinc chloride. It exhibited a strong absorption band at 420 nm and a weak absorption band at about 725 nm, as is shown in Fig. 2(a) and in Fig. 3(a), when reacted with supported zinc chloride at 60 °C for 10 min and with molten zinc chloride at about 300 °C for 5 min. The further reaction over supported zinc chloride at temperatures higher than 60 °C decreased the reflectance of the samples and altered the spectrum from that shown in Fig. 2(a) to that of Fig. 2(c). It is noteworthy in these spectra that the band at 420 nm was common, but the weak band at 725 nm disappeared with the progress of the reaction.

The treatment of porous Vycor glass alone, pretreated at 550 °C, with 9,10-dihydroanthracene at temperatures higher than 200 °C also gave a colored product. Its absorption spectrum is shown in Fig. 3(b).

The common band at 420 nm (Fig. 2(a) to (b) and Fig. 3(a)) disappeared when the products were decomposed with water. However, when the colored products obtained at higher temperatures, whose electronic absorption spectra are shown in Fig. 2(c) and Fig. 3(b), were decomposed with water, other, new colored products were recovered. The electronic absorption spectrum of the products in dichloromethane solution is shown in Fig. 3(c).

IR Absorption Spectra. Figures 4(a) and (b) are the IR absorption spectra of colored complexes of triphenylmethane and 9,10-dihydroanthracene absorbed on zinc chloride supported on porous Vycor glass platelets.

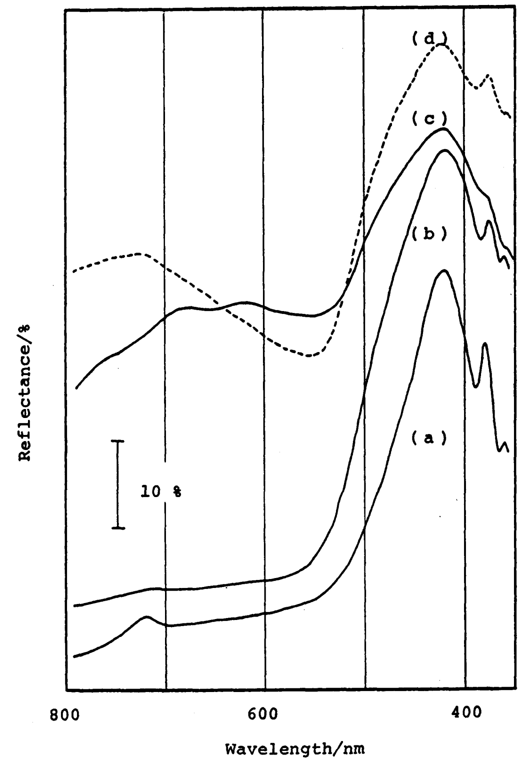


Fig. 2. Change in electronic spectra of colored products of 9,10-dihydroanthracene and anthracene on supported zinc chloride.
9,10-Dihydroanthracene; (a) at 60 °C for 10 min, (b) at 80 °C for 20 min, (c) at 100 °C for 30 min, anthracene; (d) at 60 °C for 10 min.

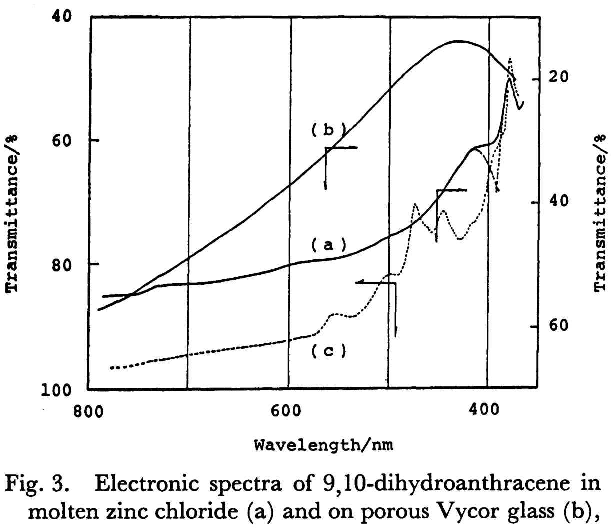


Fig. 3. Electronic spectra of 9,10-dihydroanthracene in molten zinc chloride (a) and on porous Vycor glass (b), and of polycondensed products of 9,10-dihydroanthracene formed on the supported zinc chloride and on the support (c) (in dichloromethane solution).

In these spectra, the intensity of the stretching vibration band of the aliphatic C–H relative to that of the aromatic C–H of the colored complexes seemed to be slightly smaller than that of the original molecule

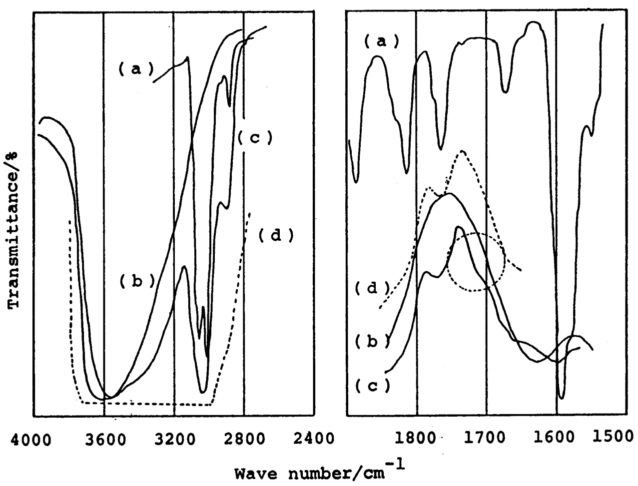


Fig. 4(a). Change in IR spectra of colored products of triphenylmethane on supported zinc chloride.
(a) Triphenylmethane on KBr, (b): zinc chloride on porous Vycor glass, (c): colored products on the catalyst after the reaction, (d) after decomposition of the colored products with water vapor.

on KBr, and the intensity of the OH groups on the silica surface increased more than that of the original. Furthermore, a very weak new absorption band appeared at about 1720 cm^{-1} for each complex. This band disappeared when the intermediates came in contact with water vapor, whereas none of the other bands, except those at 3600 cm^{-1} and 1620 cm^{-1}, changed (these two bands increased upon this water-contact).

Reaction Products. Triphenylmethane was the only identifiable product from the decomposition of its colored intermediate with water. This observation indicates that no reaction other than colored-complex formation took place on the catalyst under the present conditions.

Table 1 summarizes the analyses of the products obtained after the decomposition of 9,10-dihydroanthracene–zinc chloride colored complexes with water; these complexes had been produced by the reaction of 5 mg of the compound with 500 mg of the supported zinc chloride at various reaction temperatures for varying periods.

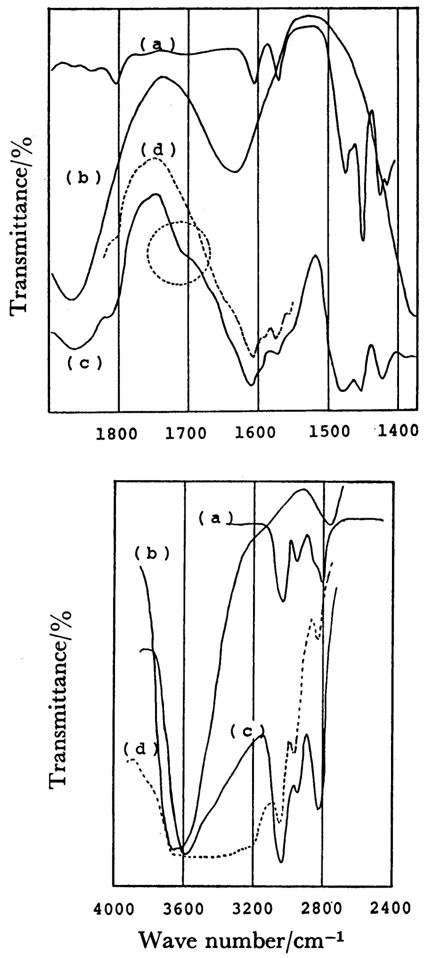


Fig. 4(b). Change in IR spectra of colored products of 9,10-dihydroanthracene on supported zinc chloride.
(a): 9,10-dihydroanthracene on KBr, (b): zinc chloride supported on porous Vycor glass, (c): colored products on the catalyst after the reaction, (d): after decomposition of the colored products with water vapor.

The electronic absorption spectra of the 9,10-dihydroanthracene-zinc chloride complexes were similar to those shown in Fig. 2(a) to (c). The products obtained below 100 °C were identified as anthracene and 1,2,3,4-tetrahydroanthracene, in nearly a 1 : 1 mol ratio. This observation indicates that the main reaction at

TABLE 1. RESULTS OF THE DECOMPOSITION OF 9,10-DIHYDROANTHRACENE OVER ZINC CHLORIDE SUPPORTED ON POROUS VYCOR GLASS

Reaction conditions: Sample/Catalyst=5mg/500 mg, Pressure 10^{-4} Torr.

Catalyst	Temp / °C	Time / min	Product distribution (wt%) 9,10-Dihydroanthracene	1,2,3,4-Tetrahydroanthracene + 1,2,3,4-Tetrahydrophenanthrene	Anthracene
Zinc chloride on Vycor glass	150	10	39.1	34.4	26.5
	100	30	59.5	19.9	20.6
	80	90	65.9	16.2	17.9
	60	90	86.7	6.2	7.1
Vycor glass	200	5	39.6	2.9	57.5

(Hydrogen gas and condensed compounds of 9,10-dihydroanthracene or of anthracene were confirmed as the other products at reaction temperatures higher than 100 °C. Although the analytical results fluctuate somewhat, they are enough to suggest the formation of some active species of 9,10-dihydroanthracene in the course of the reaction.)

temperatures lower than 100 °C is the disproportionation of 9,10-dihydroanthracene. When this substrate was treated at temperatures higher than 100 °C, hydrogen gas, anthracene dimers, and other polycondensed products, including anthracene and 1,2,3,4-tetrahydroanthracene (together with an unnegligible amount of 1,2,3,4-tetrahydrophenanthrene), were identified by gas and liquid chromatography, and by mass spectrometry. That is, at higher temperatures, the dehydrogenation of 9,10-dihydroanthracene and the condensation of 9,10-dihydroanthracene and anthracene occurred in addition to the disproportionation. The electronic spectrum of Fig. 3(c) can be attributed to some condensed polymers of 9,10-dihydroanthracene or anthracene.

The electronic-absorption spectrum of 9,10-dihydroanthracene in molten zinc chloride is reproduced in Fig. 3(a). This complex gave hydrogen gas and anthracene as the major products, in addition to 1,2,3,4-tetrahydroanthracene as a minor product. In this instance, the main reaction is the dehydrogenation of 9,10-dihydroanthracene.

9,10-Dihydroanthracene over porous Vycor glass alone pretreated at 550 °C was converted mainly to hydrogen gas and anthracene (Table 1). The main reaction is dehydrogenation.

D_2-exchanged Products. About 5 mg of triphenylmethane was treated with 600 Torr of deuterium gas at 280 °C for 3 h in the presence of 3 g of dehydrated zinc chloride. The products were $(C_6H_5)_3CD$ (15%) and HD. Similarly, 9,10-dihydroanthracene gave 13% of 9,10-dihydroanthracene-9-*d*, 8% of 1,2,3,4-tetrahydroanthracene (including deuterated derivatives), and 57% of anthracene (including deuterated derivatives). HD was also formed.

The treatment of 9,10-dihydroanthracene with 600 Torr of deuterium gas at 120 °C for 3 h over the supported zinc chloride also produced about 8% of 9,10-dihydroanthracene-9-*d*, 43% of 1,2,3,4-tetrahydroanthracene (including deuterated derivatives), 21% of anthracene (including deuterated derivatives), HD, and polycondensed products.

A glass wall or porous Vycor glass alone did not promote this D_2-exchange reaction under the same conditions.

Dissociation into Ions. The double-peaked absorption band at about 450 nm of a colored product from triphenylmethane is also present in the spectrum of the triphenylmethyl cation produced by the reaction of triphenylmethane with silica–alumina and BF_3 on silica.[10] We confirmed that HD and triphenylmethane-1-*d* were the products in the reaction of triphenylmethane with D_2 gas on the zinc chloride. These results lead us to the conclusion that the triphenylmethane absorbed on zinc chloride dissociates into ions as follows:

$$(C_6H_5)_3CH \rightleftarrows (C_6H_5)_3C^+ + H^-.$$

Portions of the hydride ions formed by this reaction may be supposed to be chemisorbed on the Lewis-acid centers of the zinc chloride catalyst, judging from a new, weak absorption band at 1720 cm^{-1} which is interpreted as arising from the Zn–H bond (Fig. 4(a)).[11]

It was also found that the IR spectrum of triphenylmethane absorbed on zinc chloride/porous Vycor glass showed a marked absorption at about 3600 cm^{-1} of the OH groups on the silica surface; this is known to be depend on hydrogen bonding between the surface hydroxyl groups and the adsorbate,[12] but H^- ions might contribute to the formation of the OH groups on the silica surface. This should further be investigated. However, triphenylmethane on zinc chloride, even if it is not supported on porous Vycor glass, substantially dissociates into ions. Therefore, the ionization of triphenylmethane on zinc chloride can be represented as follows:

$$(C_6H_5)_3CH + nZnCl_2 \rightleftarrows (C_6H_5)_3C^+(ZnCl_2)_n^-H.$$

9,10-Dihydroanthracene absorbs strongly at 420 nm and weakly at about 725 nm on the supported zinc chloride upon their first contact (Fig. 2(a)). Similarly, it gives the same absorption bands in molten zinc chloride (Fig. 3(a)).

Anthracene–zinc chloride complexes may be supposed to be formed, for anthracene was confirmed as an impurity of the sample and a reaction product. Therefore, the present band at 725 nm corresponds to that of the anthracene cation radical, for the anthracene–zinc chloride complexes absorb at 430 nm and at 730 nm (Fig. 2(d)), the absorption bands of which are assigned to the anthracene–zinc chloride EDA-complex and the anthracene cation radical respectively.[2] However, the band at 725 nm disappeared with increases in the contact time and the temperature, whereas the position of the band at 420 nm almost did not change. On the other hand, anthracene in concd H_2SO_4 impregnated with porous Vycor glass gave electronic absorption bands at 420 nm and at 725 nm, as is shown in Fig. 5. They are assigned to the 9-anthracenium ion and the anthracene cation radical respectively.[13,14] We may note here that the absorption band at 420 nm of the present complex is strikingly similar to that of the 9-anthracenium ion. Moreover, this band is distinctly different from the characteristic absorption band of the anthracene–zinc chloride EDA complex with regard to the strength of the absorption and the position of the peak. As has been mentioned above, it was found

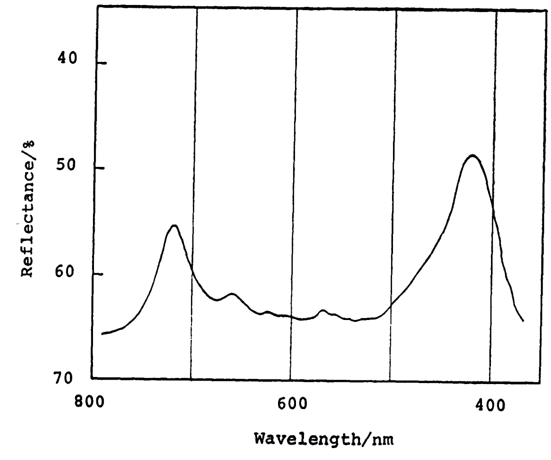
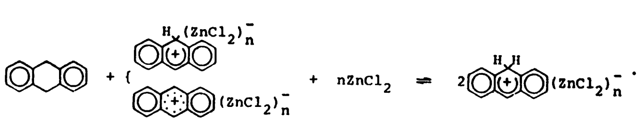


Fig. 5. Electronic spectrum of anthracene in concd H_2SO_4 impregnated with porous Vycor glass.

that aliphatic hydrogen of 9,10-dihydroanthracene is so mobile on zinc chloride that it can be exchanged with D_2 gas, that 9,10-dihydroanthracene decomposes into anthracene and 1,2,3,4-tetrahydroanthracene, and that zinc chloride abstracts the hydride ion from 9,10-dihydroanthracene. A colored 9,10-dihydroanthracene–zinc chloride complex formed on porous Vycor glass platelets also gave a weak absorption band at 1720 cm^{-1}. This can also be interpreted as an H^- ion from 9,10-dihydroanthracene being chemisorbed on Lewis acid centers of zinc chloride.

The results presented above lead us to the conclusion that 9,10-dihydroanthracene dissociates on zinc chloride as follows:

The disappearance of the anthracene cation radical at the early stage of the reaction can be explained if one assumes the following reaction:



The yellow complexes of triphenylmethane and 9,10-dihydroanthracene, which were formed at higher temperatures on porous Vycor glass pretreated at 550°C under a vacuum, are also supposed to be triphenylmethyl cations and 9-anthracenium ions respectively, but further investigation should be carried out before an assignment can be made certainly.

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