

On the Electronic Absorption Spectra and the Dipole Moment of the Molecular Compound between Stannic Chloride and Naphthalene

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Introduction

It has been well known for many years that stannic chloride as well as the halides of various metals, e.g., aluminium, boron, titanium, tin, mercury, etc., can form molecular compounds with organic compounds.⁽¹⁾⁽²⁾⁽³⁾ The organic compounds which combine with stannic chloride may be divided into two groups according to whether they contain oxygen or nitrogen atoms or not. Organic compounds of the former group, e.g., ethers, aldehydes, ketones, amines or nitrils, combine with stannic chloride with evolution of heat. On the other hand, for the latter group, composed mainly of aromatic hydrocarbons, it is known that the bond is very weak and in most cases accompanies changes of electronic absorption spectra and dielectric polarizations.

Briegleb and Kambeitz⁽⁴⁾ have, by the optical measurements, found that, in a dilute carbon tetrachloride solution, the MC's (molecular compounds) between stannic chloride and aromatic hydrocarbons exist in a 1:1 form. Ulich and his co-workers⁽⁵⁾ have measured the molecular polarization of the MC between stannic chloride and benzene, and gave 0.8D for the dipole moment of the MC, assuming that the concentration of the MC is equal to that of the stannic chloride. Strictly speaking, however, this assumption seems to be incorrect.

As for the experimental data concerning the physico-chemical properties of such MC's, not more than those described above have been reported. Also, it seems that no satisfactory theoretical explanation about the nature of the binding forces has yet been made. In an attempt to obtain more experimental knowledge which may be useful for the clarification of these problems, the present author made the following researches on the electronic absorption spectra and dielectric polarizations.

Experimental

The stannic chloride used was prepared by introducing dry chlorine into a flask which contained fused tin heated to about 350°C. The stannic chloride vapor which was generated in the flask was led, through a cooler, into another vessel. The stannic chloride thus prepared was refluxed with tin for several hours in order to convert the contained chlorine to stannic chloride. The stannic chloride thus obtained is a clear colorless liquid which shows almost a constant b.p. of 113°C. Naphthalene was recrystallized twice from methanol solutions, and dried in a vacuum desiccator containing phosphorus pentoxide for several weeks. (m.p., 80.6°C). Benzene was purified by washing with concentrated sulfuric acid, followed by fractional distillation. Ethyl acetate was dried with calcium chloride and fractionated. (b.p., 76.8°C). Cyclohexane was purified according to the method described by Hinrichsen and Kempf⁽⁶⁾.

The measurements of the absorption spectra were made by the Beckman spectrophotometer, model DU. For the measurement of the dielec-

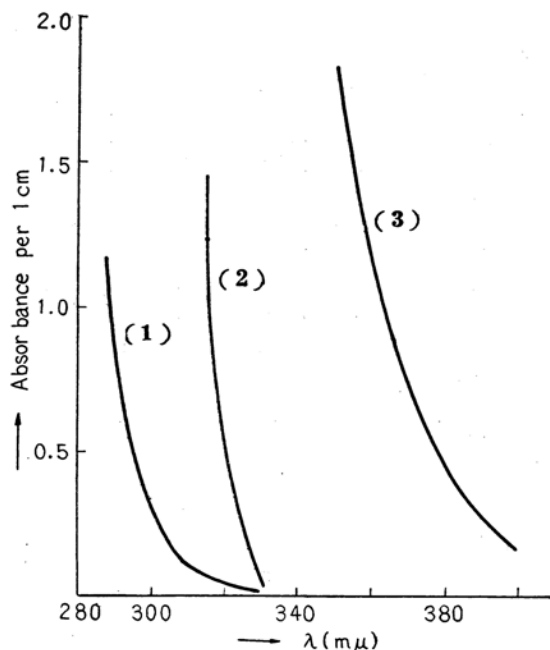


Fig. 1.—Absorption spectra of
(1) pure stannic chloride
(2) 0.0100 M naphthalene in cyclohexane
(3) 0.667 M stannic chloride and
0.0251 M naphthalene in cyclohexane.

1) Gmelins Handbuch der anorganischen Chemie, 8 Aufl., 1937, Verlag Chemie G.m.b.H., Berlin; J.W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, London, 1929.

2) P. Pfeiffer, "Die organische Molekülverbindungen," Ferdinand Enke, Stuttgart, 1927.

3) G. Briegleb, "Zwischenmolekulare Kräfte und Molekülstruktur," Ferdinand Enke, Stuttgart, 1937.

4) Ref. 3, p. 124.

5) H. Ulich, E. Hertel and W. Nespital, Z. physik. Chem., B17, 369 (1932).

6) Hinrichsen and Kempf, Ber., 45, 2106 (1912).

tric constant, the same instrument as reported by K. Kozima and T. Yoshino⁽⁷⁾ has been used in this case. Since stannic chloride is very sensitive to moisture, care was taken to protect it as far as possible during the measurements. As a very small amount of white precipitation was inevitably formed during the preparation of solutions, the solutions were transferred through a glass filter, protected from moisture, into the cells used for the absorption or dielectric measurements.

Results

1. Absorption Spectra—In Fig. 1, curves (1), (2), and (3) show the absorbance per 1 cm of stannic chloride for pure liquid state, that of naphthalene in cyclohexane and that of a mixture of stannic chloride and naphthalene in cyclo-

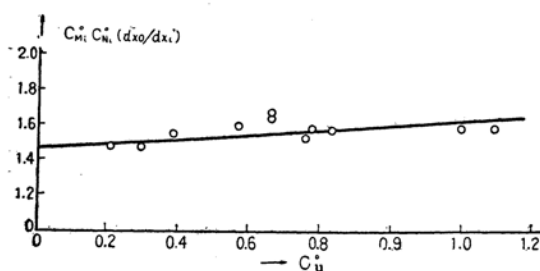


Fig. 2.

hexane, respectively. From these curves, it can be seen that, in the region of wavelength longer than 330 mμ, the absorbances of both stannic chloride and naphthalene are negligible, and so the absorbance of (3) in this region is entirely to be attributed to the molecular compound.

Next, the isothermal dilution change of the absorption of this MC was measured for eleven solutions at 18°C. It was confirmed that the results can be expressed by the following equation,

$$C_M C_N (d_{x0}/d_{x1}) = (d_{x0}/\epsilon x) C_M + d_{x0}/(\epsilon x \cdot K) \quad (1)$$

where C_M and C_N are the total concentration (in mole/l.) of stannic chloride and naphthalene (including those which are associated) for the i th solution, d_{x0}/d_{x1} is the ratio of the absorbance between zeroth and i th solutions which was derived by averaging these ratios at many different wavelengths, and ϵx and K are constants. (See Fig. 2). It may be easily proved that equation (1) can be derived from the following equation expressing the equilibrium of the 1:1 association

$$C_N/C_M(C_N - C_N) = K^* \quad (2)$$

and in fact K and ϵx appearing in (1) are the equilibrium constant and the molar absorptivity of the MC, respectively. Therefore, the results indicate that in dilute solution the concentration of the MC is governed by equation (2), in agreement with the Briegleb and Kambeitz's results. From the data, K and ϵx were determined by use of the method of least square. The results are:

$K = 0.06$ (M^{-1}), $\epsilon x = 2 \times 10^3$ ($cm^{-1} \cdot M^{-1}$) at 350 mμ. Since in this case K is very small, it seems difficult to get these values more accurately.

TABLE I

at 18°C

	x^*	d	ϵ	P_1 , cc.	$N_x \Delta P$	N_x , M/gr.	ΔP , cc
SnCl ₄	0	2.2358	2.9031	45.231	/	/	
Soln. 1	0.01070	2.2198	2.9058	/	0.00093	3.16×10^{-5}	30
Soln. 2	0.03380	2.1897	2.9131	/	0.00303	10.01×10^{-5}	30

at 40°C

	x^*	d	ϵ	P_1 , cc.	$N_x \Delta P$
SnCl ₄	0	2.1784	2.8269	45.267	/
Soln. 1	0.01070	2.1635	2.8245	/	0.00058
Soln. 2	0.03380	2.1368	2.8307	/	0.00242

* The x 's are the molarities of naphthalene calculated without assuming the formation of the MC.

2. Polarization Measurements

The dielectric constants and densities of liquid stannic chloride and two solutions of naphthalene in stannic chloride were measured at 18°C and 40°C. The results obtained are given in Table 1. The dielectric constant and density of stannic chloride itself are in good agreement with those reported by Ulich and others⁽⁵⁾. First, it was found that the polarizations of the solutions were considerably greater than the weighted means of the molecular polarizations of stannic chloride and naphthalene. This indicates that the molecular polarization of the MC is larger than the sum of those of stannic chloride and naphthalene.

In a dilute solution, it was confirmed spectrophotometrically that the MC was of 1:1 form. But in this case the situation is not quite the same because now naphthalene is dissolved in the liquid of stannic chloride. Nevertheless the author tentatively assumes here that still in this case the MC is of 1:1 form, and that the molecular polarization of the MC, P_x , is given by the following formula:

$$P_x = P_M + P_N + \Delta P \quad (3)$$

Then the polarization per one gram of the solution is given by

$$P_{12} = (\epsilon_{12} - 1)/(\epsilon_{12} + 2) \cdot d_{12} \\ = N^o_M P_M + N^o_N P_N + N_x \Delta P, \quad (4)$$

* This is an approximate equation which is exact when C_N^o is far larger than C_N . All the solutions investigated were, of course, prepared so as to satisfy this condition.

where N_x is the number of moles (per one gram of the solution) of the MC and N°_M and N°_N are those of stannic chloride and naphthalene, including the associated ones, respectively. Concerning P_M and P_N , the former was calculated from the experimental values of ϵ_M and d_M , and the latter may be taken from the experimental value reported by Briegleb⁽⁸⁾, (33.84 cc.). Thus ($N_x \Delta P$) can be determined by use of equation (4). The results obtained are given in Table 1.

The second step is to determine N_x . The concentrations of the MC in dilute cyclohexane solutions can be obtained by use of equation (2) with the K value determined from the results of isothermal dilution change. But it is clear that we cannot apply this equation to the solution for the dielectric measurement because the activity coefficient of the medium must differ in the two cases. Therefore the concentration of the MC in the solution for the dielectric measurement was estimated by comparing the absorbance of the MC in it with that in the dilute cyclohexane solution. The N_x and ΔP thus obtained are given in Table 1.

We may conclude that the orientation polarization constitutes most part of the ΔP . The dipole moment is then calculated from the averaged value of ΔP to be 1.2 D. It was found that about 80% of the naphthalene molecules were associated. It is worth while to note that the dipole moment calculated by assuming complete association is 1.0 D. This is a little larger than the corresponding value for the MC of stannic chloride with benzene reported by Ulich et al.

From Table 1, it can be seen that the $N_x \Delta P$ at 40°C is considerably smaller than that at 18°C. If we assume the dipole moment of the MC does not vary with rising temperature, ΔP should be proportional to $1/T$. In such a case we find that the N_x at 40°C is about 60–80% of that at 18°C. From this result, and by use of the reaction isochore, the heat of formation is calculated to be 2–4 kcal/mole. But this result should be regarded to be only semi-quantitative, since the agreement between these values for the two solutions was not satisfactory.

The spectra of the MC's of stannic chloride with benzene or ethyl acetate.

From the resemblance of the electronic and molecular structure of benzene and naphthalene, and also from Ulich's polarization data, it was supposed that an absorption spectrum similar to the stannic chloride-naphthalene system would occur in the stannic chloride-benzene system. In order to check this, the spectrum of a stannic chloride solution of benzene has been measured, and the result obtained was in agreement with the expectation mentioned above. (Fig. 3). A quantitative analysis was not made in this case. Simply it was observed that the absorption band of the MC was of considerably shorter wavelength than that of the stannic chloride-naphthalene system.

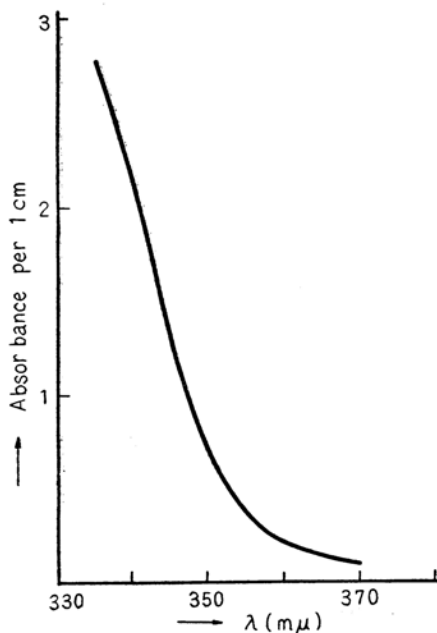


Fig. 3.—Absorption spectra of 0.187 M benzene in stannic chloride.

In an attempt to investigate the spectra of the MC's of stannic chloride with oxygenated organic compounds, ethyl acetate was chosen as an appropriate example. It was observed that much heat was evolved when stannic chloride was dissolved in it. The mixtures are clear viscous liquid and the wavelengths of their spectra are a little longer than that of stannic chloride, but considerably shorter than that of the stannic chloride-naphthalene system. The absorbance of this MC was found to be roughly proportional to the concentration of stannic chloride in the mixture. (Fig. 4).

Discussion

It is highly probable that the linkages between stannic chloride and compounds containing oxygen or nitrogen atoms are very strong, since heat is evolved when these substances are mixed. It may be supposed that these linkages are of a type of coördination linkage between the lone pair AO of oxygen or nitrogen atom and the MO of stannic chloride including the d-shell of tin atom.⁹⁾ We might explain the linkages between stannic chloride and aromatic hydrocarbons by an analogous model, basing our explanation on the fact that for many cases aromatic hydrocarbons are regarded to be of the electron-donor type. But in this case the orbital of the electron-donor molecule which interacts with that of metal halides is

8) G. Briegleb, *Z. physik. Chem.* B **16**, 276 (1932).

9) L. Pauling, *The nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, N.Y., 1940, p. 93.

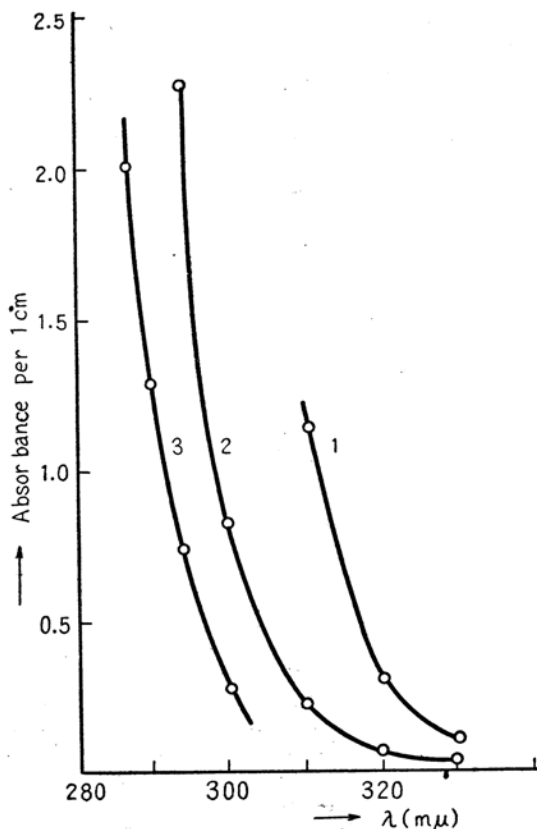


Fig. 4.—Absorption spectra of stannic chloride in ethyl acetate.

- (1) 3.57 M stannic chloride
- (2) 0.714 M "
- (3) 0.202 M "

not confined to one special atom in it, but extends throughout the whole molecule. Then the absorption spectra of such MC's may be understood as the charge-transfer spectra similar to those of the benzene-iodine complex¹⁰⁾ or quinhydrone.¹¹⁾ If this is true, the dipole moments observed for these MC's may possibly be caused mainly by the charge-transfer.*

Although the energy of the linkage in the MC between stannic chloride and ethyl ace-

tate is very different from those between stannic chloride and aromatic hydrocarbons, it must be concluded that a similar charge-transfer spectrum will exist still in the former MC. The band which was experimentally found to be proportional to the concentration of stannic chloride in the ethyl acetate solution will probably be this charge-transfer spectrum.

From the experimental results, it is likely that the wavelengths of the MC's of stannic chloride become longer as the electron-donors are varied in the sequence of ethyl acetate, benzene, and naphthalene. It is worth while to note that the lowest ionization potentials of the electron-donors become smaller in the same sequence.** The charge-transfer spectra may be roughly assigned to the transition between two energy levels formed by the perturbation between the lowest unfilled MO of the electron-acceptor and the highest filled MO of the electron-donor, and hence the wavelength of this spectrum depends largely on the energy difference between the original unperturbed MO's.¹¹⁾ Now it is clear that such energy differences become larger, the larger the ionization potentials of the electron-donor. Thus, the relation between the ionization potentials of the electron-donors and the wavelengths of the MC's may be explained by the previously given MO theory.

Summary

The 1:1 form of the molecular compound between stannic chloride and naphthalene in dilute solution has been confirmed by the measurements of electronic absorption spectra. The exaltation of the molecular polarization of this molecular compound has been determined from both optical and dielectric measurements and the dipole moment has been calculated from it. The absorption spectra of other similar molecular compounds have also been measured. It has been proposed that the intermolecular linkages may be explained as the charge-transfer bond.

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10) R.S. Mulliken, *J. Am. Chem. Soc.*, **74** 811 (1952).

11) H. Tsubomura, *This Bulletin*, **26**, 304 (1953).

* Briegleb took the dipole moment of such MC's as were caused by the deformation of stannic chloride molecule from the tetrahedral structure. (ref. 3, p. 84). It seems that such a cause should also be taken into account as an additive factor of the dipole moment of these MC's. But his explanation for the original nature of the bonds in these MC's seems to be unsuccessful.

** This fact was kindly suggested to the author by Dr. S. Nagakura.