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Note

Heat of formation of an intercalated complex between iron (III) oxychloride and pyridine

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A layered FeOCl crystal forms an intercalated complex with pyridine. On complexation with pyridine, the crystal changes in basal spacing from 7.9 to 13.5 Å, and in color from purple to black[1], and increases in electric conductance[2] by a factor of 10^7. In an effort to understand this complexation phenomenon, the present study is concerned with the heat of formation and the adsorption process of pyridine on FeOCl.

EXPERIMENTAL

Materials

Iron(III) oxychloride was synthesized from anhydrous $FeCl_3$ and α-Fe_2O_3. The mixture with a molar ratio $FeCl_3/Fe_2O_3 = 3/2$ was evacuated and sealed in a Pyrex glass tube, followed by heating at 400 for several days. Then, the resulting crystals of FeOCl were purified by washing with acetone to remove extra $FeCl_3$. After drying by evacuation, the crystals were sieved to obtain a fraction of 30–60 mesh. Pyridine was purified by distillation in an atmosphere of nitrogen after refluxing with NaOH granules for 6 h.

Method

A commercial twin type microcalorimeter (Oyo-denki CM-502) was used for the measurement of immersion heat. The calorimeter assembly consisted of two stainless steel vessels having 50 ml fluid capacity. Each vessel was filled with 40 ml of purified pyridine. FeOCl was sealed in a Pyrex glass bulb after evacuation at 100 °C for 2 h. A sample bulb and an empty one for reference were allowed to stand overnight in the calorimeter system to attain thermal equilibrium at a given temperature. Then, the two bulbs were broken at the same time in the corresponding vessels and the heat evolved on immersion of FeOCl in pyridine was recorded. The recording was repeated on varying sample weights in order to assess the heat due to slight dissolution of FeOCl in pyridine at three immersion temperatures, 24, 28.5, and 40 °C.

After the completion of each run, FeOCl crystals immersed in pyridine were separated by filtration in flowing dry nitrogen to avoid moisture in the atmosphere. The filtration was carried out using a Teflon filter to prevent contamination with filter paper. The change in basal spacing of FeOCl before and after the immersion in pyridine was observed by an X-ray diffractometer using Ni-filtered Cu-Kα radiation. The amount of vapor pyridine adsorbed on FeOCl was followed gravimetrically by measuring the extension of a quartz spring suspending a given amount of FeOCl.

RESULTS AND DISCUSSION

The total heat evolved on immersion of FeOCl of varying weight is shown in Fig. 1. According to the least square method, the slope and the intercept at zero sample weight of the line indicated in the figure were determined to be 38.14 ± 0.73 cal g^{-1} (i.e., 4.09 ± 0.08 kcal mol^{-1} of FeOCl) and 0.05 ± 0.24 cal, respectively. These results show that the evolved heat was directly proportional to the sample weight and not influenced by the change in immersion temperature in the observed region.

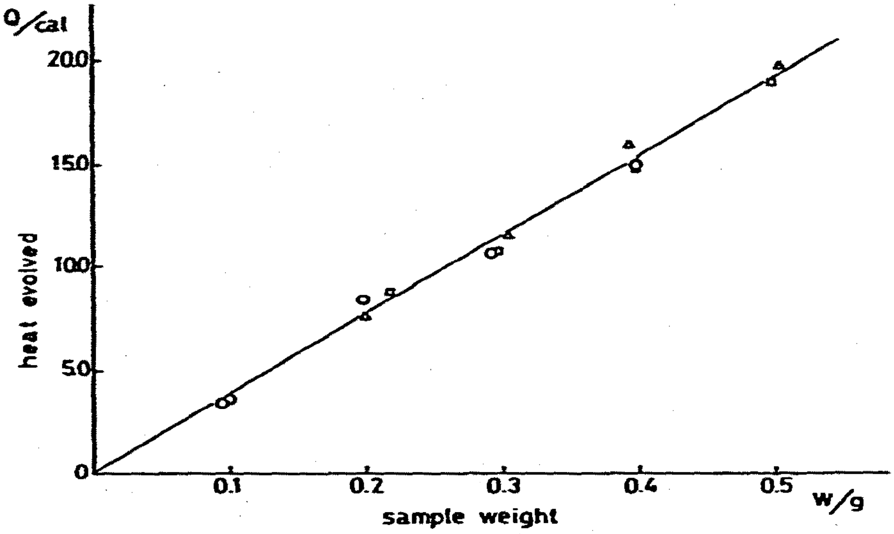

Fig. 1. Heat evolved on immersion of varying sample weights at: (O), 24 °C; (Δ), 28.5 °C; (□), 40 °C.

Figure 2 shows the adsorption behavior of pyridine on FeOCl under the relative vapor pressure of 0.65 at 30 °C. The adsorption equilibrium was attained at 0.33 mol of pyridine per mol of FeOCl. This amount of pyridine could not be removed even on prolonged evacuation at 10^{-3} torr. When FeOCl was exposed to pyridine under the saturated vapor pressure at 30 °C, the adsorption exceeded 0.33 mol per mol of FeOCl within 15 min. However, the

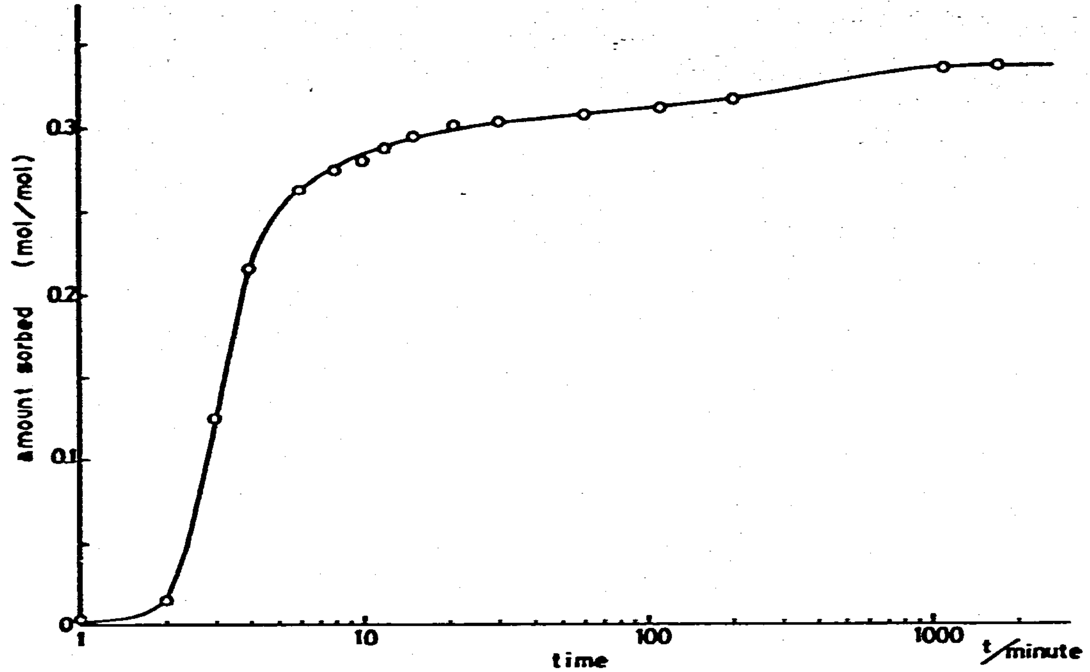

Fig. 2. Adsorption behavior of pyridine on FeOCl under the relative vapor pressure of 0.65 at 30 °C.

excess amount of pyridine was readily removed by evacuation. The additional amount of pyridine can be attributed to surface condensation.

After the measurement of immersion heat in pyridine, FeOCl changed in color from purple to black and X-ray diffraction data showed that the initial FeOCl had completely changed into the complex with a basal spacing 13.5 Å. The C, H, N elemental analysis of FeOCl immersed in pyridine revealed that 1/3 mol of pyridine had reacted with one mol of FeOCl like the complex formed by the reaction of vapor pyridine. Found: C, 13.90±0.05; H, 1.19±0.02; N, 3.40±0.03%. Calcd. for $FeOCl(C_5H_5N)_{1/3}$: C, 14.95; H, 1.25; N, 3.49%.

The analytical data are slightly lower in %C than the calculated value. This is attributed to the incomplete combustion of pyridine adsorbed in the interlayer region of FeOCl, and well encountered in the course of studies on intercalated complexes[3]. These results lead to the conclusion that FeOCl forms a stable complex by the reaction with liquid as well as vapor pyridine, the composition of which is $FeOCl(C_5H_5N)_{1/3}$.

As shown in a previous paper[1], pyridine is arranged with the principal molecular axis perpendicular to the FeOCl layer in the interlayer region. Thus, it is reasonable to assume some interaction between the non-bonding orbital of nitrogen in pyridine and the σ orbital of chlorine, like the interaction in the usual n-σ type charge-transfer complexes of pyridine and halogens. The heat of formation of the Cl---N pair is estimated to be 12.27±0.24 kcal mol^{-1} which is three times the heat of formation of $FeOCl(C_5H_5N)_{1/3}$, 4.09±0.08 kcal mol^{-1} determined in the present study. This value is compared with the heat of formation of the donor–acceptor pairs of pyridine–halogen complexes in Table 1. The present value for the Cl---N pair is larger than those for the other pyridine–halogen pairs. This can be interpreted in terms of the larger acceptor strength of chlorine than those of bromine and iodine, and is in accordance with the simplified charge-transfer theory by Mulliken[4]. The present finding suggests that the formation mechanism of the FeOCl complex of pyridine is similar to that of usual n-σ type molecular complexes.

TABLE 1

HEAT FORMATION OF PYRIDINE–HALOGEN COMPLEXES

	$-\Delta H$ *(kcal mol^{-1})*	*Solvent*	*Ref.*
Py-I_2	7.8	1,2-dichloroethane	5
	7.8	n-heptane	6
Py-Br_2	10.3	1,2-dichloroethane	5
Py-(ClOFe)	12.27±0.24		

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