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THERMAL ANALYSIS OF HOFMANN'S PYRROLE, THIOPHENE, BENZENE, PHENOL, AND ANILINE CLATHRATES $Ni(NH_3)_2Ni(CN)_4.2G$ BY DIFFERENTIAL SCANNING CALORIMETRY

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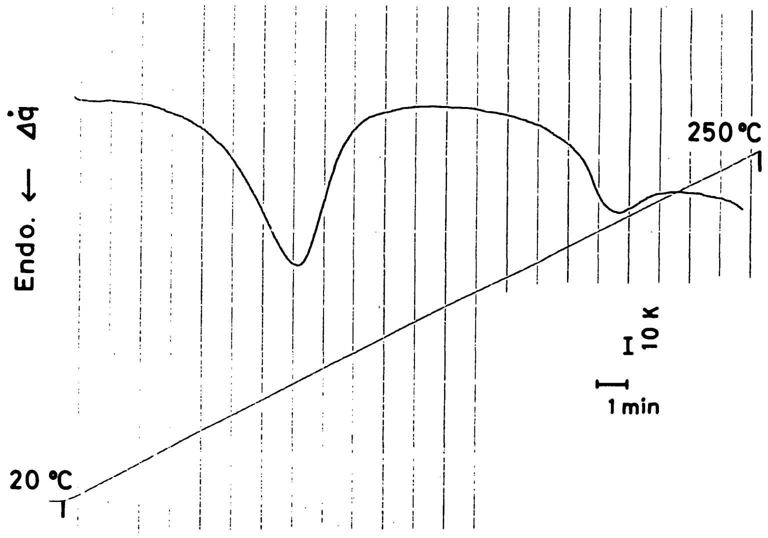
Hofmann's clathrates $Ni(NH_3)_2Ni(CN)_4.2G$ (G = C_4H_5N, C_4H_4S, C_6H_6, C_6H_5OH, or $C_6H_5NH_2$) were analyzed by differential scanning calorimetry. The analytical conditions were examined and the enthalpy changes accompanied with the liberation of guest molecules were determined for these clathrates except the aniline one.

As part of synthetic study on the Hofmann-type and analogous clathrates[1,2] we have been beginning on systematic investigations of their thermoanalytical behavior. This communication reports on our first examination concerned with differential scanning calorimetry (DSC) of Hofmann's clathrates $Ni(NH_3)_2Ni(CN)_4.2G$ with the guest G = C_4H_5N, C_4H_4S, C_6H_6, C_6H_5OH, or $C_6H_5NH_2$. With regard to thermoanalytical investigations of the Hofmann-type and analogous clathrates, a few papers have been published by other groups[3-6]; Ohyama et al.[5] described the process of thermal decomposition in detail using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA). Hofmann's benzene clathrate, for example, has been reported to liberate the guest molecules on heating by 120 °C in an nitrogen stream leaving the residual host $Ni(NH_3)_2Ni(CN)_4$; the enthalpy change, 55 kJ mol^{-1}(C_6H_6), was estimated from the analysis of the DTA curve recorded for the sample specimen of 400-500 mg with the heating rate 1 K min^{-1}. Since the quantity of sample is critical to assure rapid and uniform propagation of heat during a dynamic thermoanalytical measurement, the high-sensitive DSC technique applied in this experiment, using the sample quantities of a few milligrams, appears to be superior to calssical DTA in obtaining reliable thermal parameters.

The clathrates used in this experiment were prepared by leaving the ammoniacal solution of nickel(II) chloride and potassium tetracyanonickelate(II) and the organic phase of the guest species diluted in xylene in contact for a few days or weeks in a refrigerator. Fine crystals obtained were identified by infrared spectroscopy, powder X-ray diffractometry, and chemical analysis; the products left after thermal decomposition in open holders were analyzed by the same techniques. The crystal freshly prepared were finely powdered and subjected to the measurement using a Daini-Seikosha Model SSC-560-S heat-flux differential scanning calorimeter. DSC curves were recorded from room temperature to 250 or 350 °C under ambient atmosphere for various amounts (1 - 4 mg) of sample specimens in open aluminium holders (ca. 65 mg with 6 mm inner diameter and 5 mm depth) or in sealed aluminium holders (ca. 210 mg with 15 μl capacity); a blank open or sealed holder was used as



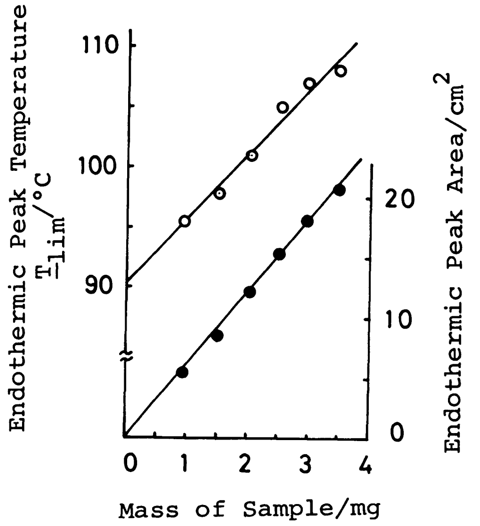
Mass of sample: 3.08 mg
Heating rate: 10 K min^{-1}
Chart speed: 1 cm min^{-1}

Figure 1. The DSC curve of $Ni(NH_3)_2Ni(CN)_4.2C_6H_6$ in the open holder.

the reference. Each holder was baked up to 350 °C before use. The calorimeter was calibrated with the NBS-ICTA GM-758 reference materials. The heating rates 2.5, 5, 10, 15, and 20 K min^{-1} were examined in order to check the reproducibility and the linearity against mass of samples; the rate 10 K min^{-1} was chosen as the most appropriate.

As exemplified in Fig. 1, an endothermic peak appeared at first accompanied with liberation of the guest molecules for the pyrrole, thiophene, benzene, and phenol clathrates in the open holders; the second one was due to liberation of the ammonia molecules from the residual host $Ni(NH_3)_2Ni(CN)_4$. In the case of the aniline clathrate, the liberation of guest molecules was incomplete at the first stage and the rest was released along with the ammonia molecules at the second stage. These observations are consistent with those described in the previous papers.[3-6] The enthalpy change accompanied with the liberation of guest molecules was calculated from the area of the first endothermic peak determined by Simpson's rule. As shown in Fig. 2, the linear relationship between the area and the mass of sample specimens has been observed with the correlation coefficient of 0.999 for the benzene clathrate; the similar relationship has also been observed for the other clathrates except the aniline one. The values of the enthalpy change listed in Table I were calculated from the least-squares fitting of the data measured for the samples in the open holders with the heating rate of 10 K min^{-1} and the chart speed 1 cm min^{-1}.

Another conventional parameter, limiting peak temperature, was determined by the least-squares calculation as the peak temperature extrapolated to infinitesimal mass of the sample specimen: the linearity with the correlation coefficient of 0.986 has been obtained for the benzene clathrate exemplified in Fig. 2. The limiting peak temperature can be seen as a characteristic parameter in comparing the thermal behavior of the substantially isomorphic Hofmann's and Hofmann-type



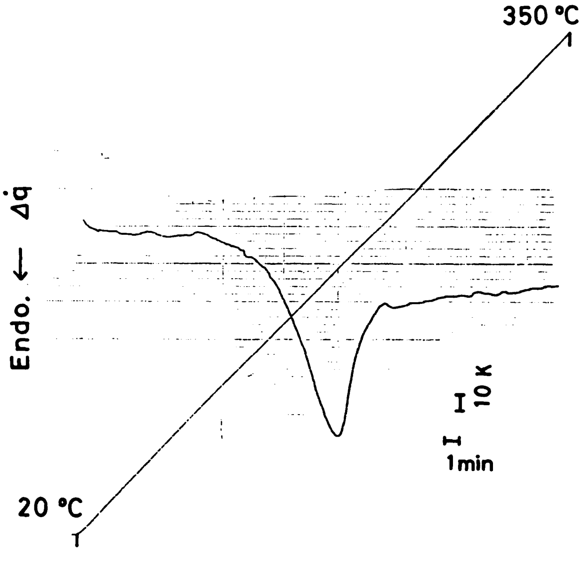
Heating rate: 10 K min^{-1}

Chart speed: 1 cm min^{-1}

Figure 2. Plots of area of endothermic peak (solid circles) and peak temperature (open circles) vs. mass of sample for $Ni(NH_3)_2Ni(CN)_4.2C_6H_6$ in the open holders.

clathrates under a given condition, although it cannot have an explicit thermodynamical meaning. The values of the limiting peak temperatures are also listed in Table I.

The change of internal energy accompanied with the liberation of guest molecules from the benzene clathrate was measured in the sealed holders. A typical DSC curve is shown in Fig. 3. The value calculated from the area of the peak by the least-squares method 33 kJ mol^{-1} agreed with the difference in the values between the enthalpy change measured in the open holder and the work done by the liberated benzene molecules in the sealed holder at the limiting peak temperature



Mass of sample: 3.50 mg
Heating rate: 10 K min^{-1}
Chart speed: 0.5 cm min^{-1}

Figure 3. The DSC curve of $Ni(NH_3)_2Ni(CN)_4.2C_6H_6$ in the sealed holder.

TABLE I. Enthalpy change, $\Delta\underline{H}$, and limiting peak temperature, $\underline{T}_{\mathrm{lim}}$, for $\mathrm{Ni(NH_3)_2Ni(CN)_4\cdot 2G}$*

G	$\Delta\underline{H}$/kJ $\mathrm{mol^{-1}}$	$\underline{T}_{\mathrm{lim}}$/K
C_6H_6	36 ± 3 (0.999)	363 ± 2 (0.986)
C_4H_4S	36 ± 5 (0.993)	360 ± 2 (0.987)
C_4H_5N	46 ± 7 (0.999)	399 ± 3 (0.999)
C_6H_5OH	50 ± 9 (0.994)	421 ± 3 (0.990)

* The range of 90 % confidence, and the correlation coefficient obtained for the least-squares fitting (in the parentheses) are shown for each value.

169 °C. Therefore, the values of enthalpy changes measured in the open holders are quite reliable.

The values of the enthalpy change and the limiting temperature are larger for the guest species with higher boiling point in its neat liquid. The tendency is consistent with the qualitative observation of the apparent stability for Hofmann-type clathrates under ambient conditions. Sooner decomposition of the clathrate has been observed, when it has the guest species with a lower boiling point in its neat liquid.[1)] The values of the enthalpy change are comparable with the heats of evaporation for the respective guest species. The value for the benzene clathrate 36 kJ $\mathrm{mol^{-1}}$ is about 2/3 times that previously observed by DTA.[5)] Because the sum of the internal energy change and the $\underline{p}\Delta\underline{V}$ work agrees with the enthalpy change observed in this experiment, the previous value should have been overestimated. With respect to the limiting peak temperature, it decreases by decreasing the heating rate. However, any definite relationship which might make it possible to extrapolate the temperature to the infinitesimal heating rate has not yet been found out. The relationship between the thermal parameters and the structure of the clathrate will be discussed elsewhere.[7)]

References

1) T. Iwamoto, Isr. J. Chem., 18, 240 (1979).
2) T. Iwamoto, J. Mol. Struct., 75, 51 (1981).
3) J. Leicester, J. K. Bradley, and R. G. Burr, Chem. Ind. (London), 1962, 208.
4) Y. Mathey and C. Mazieres, Bull. Soc. Chim. Fr., 11, 2918 (1973).
5) J. Ohyama, R. Tsuchiya, A. Uehara, and E. Kyuno, Bull. Chem. Soc. Jpn., 50, 410 (1977).
6) A. Sopkova and J. Bubanec, J. Therm. Anal., 12, 94 (1977).
7) I. Uemasu and T. Iwamoto, submitted to the 2nd International Symposium on Clathrate Compounds and Molecular Inclusion Phenomena, Parma, August-September 1982; the paper will be published in Journal of Inclusion Phenomena in 1983.

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