Thermal Behavior of the Clathrate Compounds of the Type $M(diam)M'(CN)_4 \cdot 2C_6H_6$

Jun-ichi Ohyama, Ryokichi Tsuchiya, Akira Uehara, and Eishin Kyuno*

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

**Department of Pharmaceutical Science, School of Pharmacy, Hokuriku University, Kanazawa 920*

(Received August 25, 1976)

The thermal behavior of the guest molecule trapped in the clathrate compounds, $M(diam)M'(CN)_4 \cdot 2C_6H_6$, where M and M′ are bivalent metal atoms and diam is two ammonia molecules or one molecule of diamine, and the structural changes of the host lattice upon heating were studied by means of derivatographic and isothermal measurements. In $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$, the elimination of guest benzene molecules was found to proceed in two steps. X-Ray powder diffraction patterns suggest that the skeleton of the host is preserved, at least during the first liberation of 1 mol of benzene, but the skeleton collapses after the complete liberation of benzene and ammonia. The host skeleton of $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ was preserved till the liberation of 75% of benzene. The activation energies were a little larger than the respective enthalpy changes. The replacement of M′=Ni by Pd or of M′=Cd by Hg in the clathrate compounds, if M and diamine are the same, scarcely changes the activation energy for the liberation of the guest molecule, but the replacement of M and diamine by other ones somewhat changes the activation energy.

A well-known clathrate compound, $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$, was first prepared by Hofmann and Küspert in 1897.[1] They pointed out that the benzene molecule in this compound is retained firmly as a guest in the host lattice, and its elimination cannot be detected at room temperature under ordinary pressure. Anysley *et al.*[2] reported, however, that the benzene molecule can be removed slowly *in vacuo* even at room temperature without the liberation of ammonia from the lattice. The crystal structure of this clathrate compound was determined by means of X-ray diffraction by Powell and Rayner,[3,4]

By replacing both or either one of the nickel ions in $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ by other bivalent metal ions which can form hexacoordinated, octahedral and tetracoordinated, square planar complexes, various modified compounds have been prepared and their structures were confirmed to be similar to that of $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.[5-10]

In analogous clathrate compounds such as $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$[11] the ethylenediamine molecule links both cadmium ions in upper and lower adjacent layers, forming three-dimensional host lattice network.[12,13]

All the compounds containing the square planar $M'(CN)_4$ (M′=Ni or Pd) moiety may be referred to "Hofmann-type clathrates." Recently, another new type of clathrate compounds containing tetrahedral $M'(CN)_4$ moiety was prepared by Iwamoto and others and the crystal structures were determined.[14-16] These compounds are called "Iwamoto-type clathrates" to distinguish them from the Hofmann-type ones.

Aynsley *et al.* examined the thermal decomposition of $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$, and found that the elimination of benzene proceeds in the zeroth order,[2] which indicates that the rate determining step is the escape of benzene molecule from the surface of the clathrate. On the other hand, it is known that the rate of the escape of benzene varies with the kind of metal atom constituting the host lattice.[2] The present study was undertaken (1) to investigate the thermal liberation processes of benzene molecule from the host lattices in the two types of clathrate compound and (2) to see what effect is induced by the variation of the host lattices.

Experimental

Preparation of Clathrate Compounds. The clathrate compounds $M(diam)M'(CN)_4 \cdot 2C_6H_6$, where M is Cd, Ni or Cu, (diam) is $(NH_3)_2$, ethylenediamine or trimethylenediamine and M′ is Ni, Pd, Cd, and Hg, were prepared[5-7,11,14] and their characterization was carried out by measuring both IR spectra and X-ray powder diffraction patterns.

$Cd[Ni(CN)_4]$ was prepared by a method similar to that for $Zn[Ni(CN)_4]$, and dried at 70 °C for 2 h. The compound was used as the reference material to examine the final product by the thermal decomposition of $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$. Found: C, 17.74; N, 20.39%. Calcd for $Cd[Ni(CN)_4]$: C, 17.45; N, 20.35%.

One of the compounds corresponding to the host lattice which has lost the guest molecule $Cu(NH_3)_2Ni(CN)_4$, was obtained by keeping the mother clathrate $Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ to stand in an ambient atmosphere for a few days.[17]

Measurements. The derivatograms for these compounds were obtained with a MOM Derivatograph Typ-OD-102. 0.5 or 0.4 g of sample was used in each run. All the measurements were carried out under a constant flow of nitrogen stream with a heating rate of 1 K min^{-1}. The enthalpy changes, ΔH, were evaluated by the analysis of DTA peak in the derivatogram.[18]

The isothermal measurements were carried out with a Shimadzu TM-1A Thermanobalance in static air.

The infrared and far infrared absorption spectra in the Nujol and HCB mull states were measured with JASCO IRA-2 and IR-F infrared spectrophotometers, respectively.

The X-ray powder diffraction patterns were recorded with a Rigaku-denki Geiger-flex X-ray Analyser, using Cu$K\alpha$ ray (λ=1.5405 Å) filtered with a nickel plate.

Results and Discussion

Hofmann-type Clathrate Compounds. *Derivatography*: The derivatograms of $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (I), $Cd(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$ (II), $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ (III), and $Cd(en)Pd(CN)_4 \cdot 2C_6H_6$ (IV) are shown in Fig. 1. The TG curve of compound I indicates that the mass loss of 1 mol of benzene was observed until 130 °C, and then another 1 mol of benzene and 2

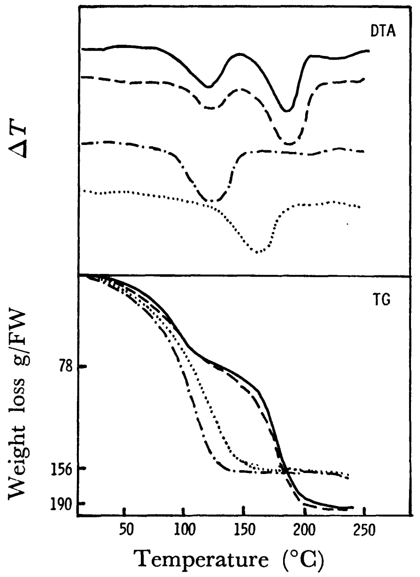

Fig. 1. Derivatograms of compounds (I) $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (——), (II) $Cd(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$ (----), (III) $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ (-·-·-) and (IV) $Cd(en)Pd(CN)_4 \cdot 2C_6H_6$ (······).

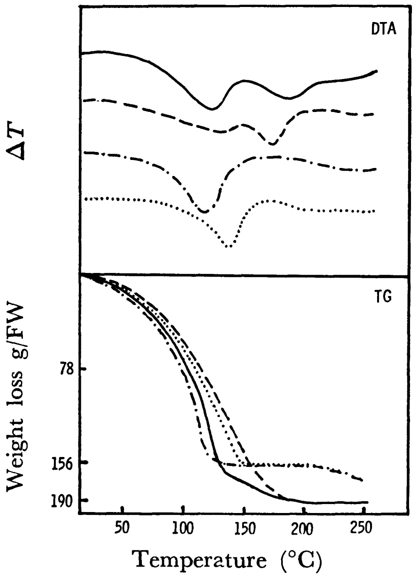

Fig. 2. Derivatograms of compounds (V) $Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (——), (VI) $Cu(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$ (----), (VII) $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (-·-·-) and (VIII) $Ni(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$ (······).

mol of ammonia were lost successively in the higher temperature region 135—200 °C, no further mass loss being detectable up to the decomposition point. The elemental analysis for the product obtained by heating I at 200 °C is as follows: Found: C, 17.52; N, 20.00%. Calcd for $CdNi(CN)_4$: C, 17.45; N, 20.35%. The DTA curve gives two endothermic peaks corresponding to the discrete mass loss steps.

Compound II gives only one mass loss step in TG, but shows two split endothermic peaks in DTA. It seems that two benzene molecules are eliminated in two overlapping steps.

On the other hand, compounds III and IV lose the benzene molecules in one step up to 130 °C and 140 °C, respectively, each giving an endothermic peak at the corresponding region in the DTA curve. Ethylenediamine was not liberated until the decomposition point. The elemental analysis for the product obtained by heating compound III at 140 °C is as follows: Found: C, 21.67; H, 2.49; N, 24.35%. Calcd for $Cd(en)Ni(CN)_4$: C, 21.48; H, 2.39; 25.06%.

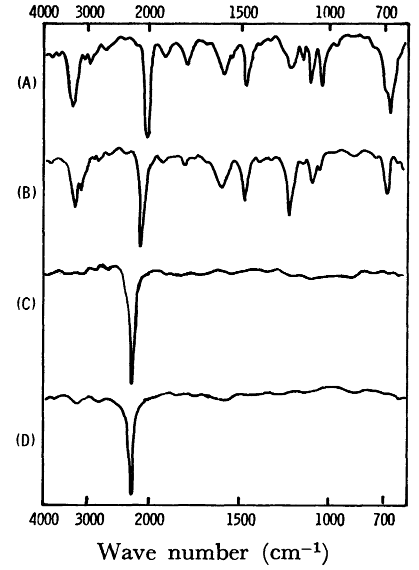

Fig. 3. IR spectra of compound (I) (A), the product obtained by heating (I) at 130 °C (B), that obtained at 200 °C (C) and of $Cd[Ni(CN)_4]$ (D).

Figure 2 shows the derivatograms of $Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (V), $Cu(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$ (VI), $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ (VII) and $Ni(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$ (VIII). In compound V, the TG curve shows two steps of mass loss at 130 °C and at 130—175 °C, the corresponding discrete peaks appearing in the DTA curve. From the results of infrared absorption spectral measurements, the first step is considered to correspond to the elimination of 2 mol of benzene and the second to the liberation of ammonia. The total weight loss due to the escape of all the benzene and ammonia is also observed in compound VI, the separation of their two processes not being clear.

Both compounds VII and VIII lost all benzene in one step. The weight remained constant till 250 °C at which the partial liberation of ammonia was observed just before the decomposition point.

IR and Far-IR Spectra. In order to clarify the structural change at several stages upon heating, changes in the infrared and far-infrared absorption spectra and X-ray diffraction patterns were measured for compounds I and III.

The infrared absorption spectra of compound I heated at various temperatures are shown in Fig. 3, together with that of $Cd[Ni(CN)_4]$, which is expected to be formed by heating compound I. The spectrum of I in which one mole of benzene is lost at 130 °C is similar to that of the starting compound at room temperature except for the weakened bands assigned to benzene at 3072, 3055, 3019, 1972, 1872, and 1479 cm^{-1}.[14] At 200 °C, however, the bands assigned to

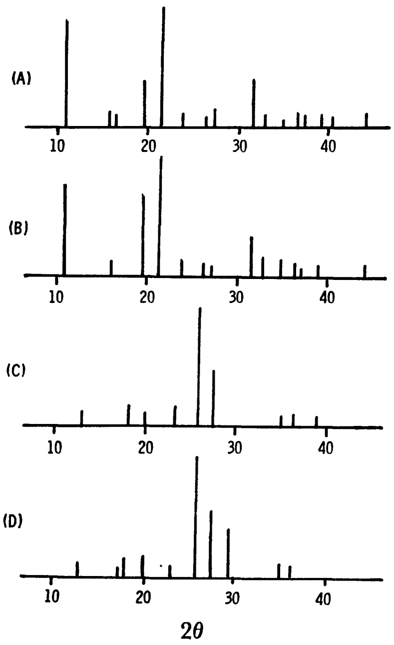

Fig. 4. X-Ray diffraction patterns of compound (I) (A), the product obtained by heating (I) a 130 °C (B), that obtained at 200 °C (C) and of Cd[Ni(CN)$_4$] (D).

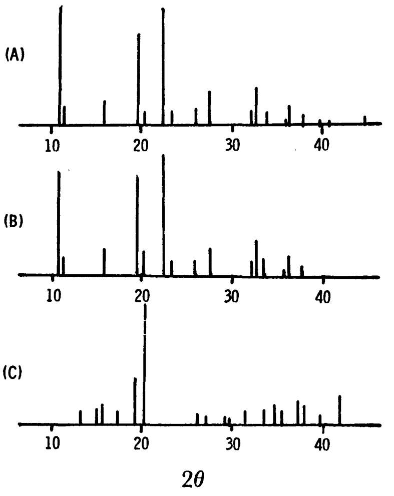

Fig. 5. X-Ray diffraction patterns of compound (III) (A), the product obtained by heating (III) at 120 °C (B) and that obtained at 140 °C (C).

benzene and to ammonia disappear, and the C≡N stretching vibration band is shifted to *ca.* 20 cm^{-1} higher. The spectrum coincides with that of Cd-[Ni(CN)$_4$]. This supports the elimination processes of benzene and ammonia.

In compound III, the bands assigned to benzene disappear completely at 140 °C, accompanied by the elimination of benzene at this temperature. So far as the ethylenediamine is concerned, the band due to NH$_2$ wagging mode (*ca.* 1089 cm^{-1}) disappears and two new bands (*ca.* 1120, 1065 cm^{-1}) appear upon heating. The results suggest that the structure of ethylenediamine molecule bridging between the layers of M(CN)$_4$ network changes to some extent. The fact that the band due to CH$_2$ rocking vibration at 856 cm^{-1} still remains after heating suggests that the

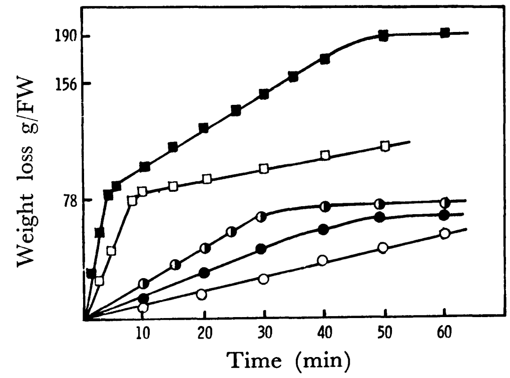

Fig. 6. The plots of weight loss *vs.* time for compound (I).
○: 84 °C, ●: 94 °C, ◑: 104 °C, □: 138 °C, ■: 160 °C.

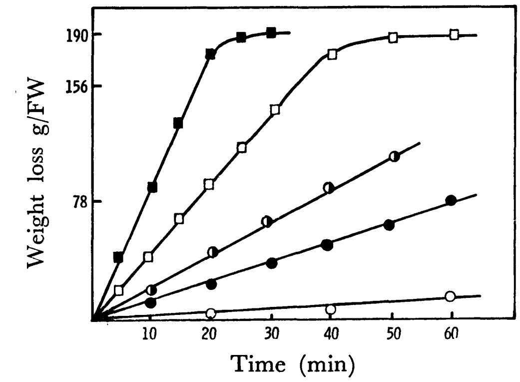

Fig. 7. The plot of weight loss *vs.* time for compound (III).
○: 55 °C, ●: 80 °C, ◑: 89 °C, □: 100 °C, ■: 119 °C.

trans configuration of ethylenediamine remains unchanged.[19]

X-Ray Powder Diffraction Patterns. The X-ray powder diffraction patterns for compound I obtained in each heating step are shown in Fig. 4. The pattern obtained at 130 °C shows no change from that at room temperature, but at 200 °C the pattern completely changes to give a similar one to that of Cd[Ni(CN)$_4$]. This suggests that the crystal lattice of compound I at room temperature is retained even when one mole of benzene is lost but the lattice is deformed at first when another one mole of benzene and ammonia are liberated.

The change in the X-ray patterns for compound III is shown in Fig. 5. The pattern at room temperature remains till 120 °C at which 75% of benzene is removed, but it becomes quite different at 140 °C at which the residual benzene is completely evolved.

Isothermal Kinetics. The weight losses of the compounds *versus* time of heating at various temperatures for compounds I and III are plotted in Figs. 6 and 7, respectively.

In compound I the elimination of 1 mol of benzene proceeds in the zeroth order at least at temperature below 130 °C, but above 130 °C the remaining benzene and ammonia are liberated more slowly also in the zeroth order after 1 mol of benzene is removed,

TABLE 1. ENTHALPY CHANGES ΔH AND ACTIVATION ENERGIES E_a IN THE ELIMINATION OF BENZENE MOLECULE FROM CLATHRATE COMPOUNDS

Compound		ΔH kJ mol^{-1}	E_a kJ mol^{-1}
I	$Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_5$	59	75.6 (1st step) 71.0 (2nd step)
II	$Cd(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$	55	74.8 (1st step)
III	$Cd(en)Ni(CN)_4 \cdot 2C_6H_6$		51.2
IV	$Cd(en)Pd(CN)_4 \cdot 2C_6H_6$	50	51.7
V	$Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$	50	65.9
VI	$Cu(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$		67.2
VII	$Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$	55	67.2
VIII	$Ni(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$	55	67.6

The results suggest that 2 mol of benzene are liberated in two different mechanisms. However, since the two guest benzene molecules cannot be distinguished from each other in their structure, it is considered that a thermally metastable intermediate might be formed after the loss of one mole of benzene retaining the initial host lattice.

On the other hand, the elimination of benzene from the clathrate III is considered to proceed in the zeroth order up to 80% removal of benzene as seen in Fig. 7. The rate constant k for the elimination of benzene was obtained from the slope of the lines shown in Figs. 6 and 7. The activation energies E_a were calculated from the Arrhenius plots (Table 1). The enthalpy changes ΔH, calculated by the analysis of the DTA curve, are also given.

The enthalpy changes are about 55 kJ mol^{-1} in all the clathrates and the activation energy values are relatively similar to one another within 66—75 kJ mol^{-1} except for those of III and IV. This suggests that the elimination process is analogous to that of the vaporization of the liquid so that the migration of the benzene molecule within the lattice is comparatively easy and the rate determining step is the escape of the benzene from the surface, giving the zeroth order. From a comparison of E_a values we see that the replacement of the tetracoordinated metal atom from nickel to palladium causes no appreciable change. On the other hand, replacement of the hexacoordinated metal or amine with others gives rise to some changes in E_a values.

The values for compounds III and IV which contain ethylenediamine as the diamine are slightly smaller than those for other compounds which contain ammonia as the diamine. It can be seen that the steric repulsion between ethylenediamine and the benzene molecule makes it unstable for benzene to exist in the cavity of the host lattice, owing to the replacement of a more bulky ethylenediamine instead of two ammonia molecules.

Iwamoto-type Clathrate Compounds. *Derivatography*: The derivatograms of $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$ (IX), $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$ (X), $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ (XI), and $Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$ (XII) are shown in Fig. 8. IX gives two steps of mass loss up to 120 °C and 120—150 °C in TG and two endothermic peaks corresponding to each step in DTA curve. From the infrared absorption spectra, it seems that the first step of mass loss is due to the elimination of 2 mol of benzene and the second to the liberation of ammonia, resembling the elimination process in compound V.

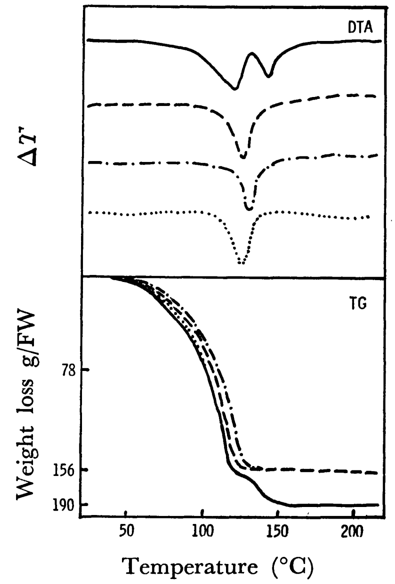

Fig. 8. Derivatograms of compounds (IX) $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$ (——), (X) $Cd(en)Hg(CN)_4 \cdot 2C_6H_6$ (----), (XI) $Cd(en)Cd(CN)_4 \cdot 2C_6H_6$ (-·-·-) and (XII) $Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$ (······).

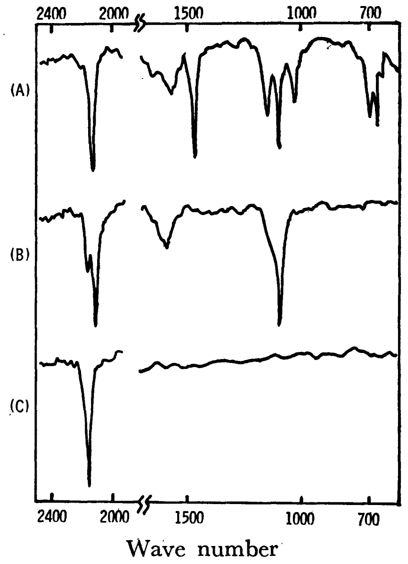

Fig. 9. IR spectra of Compounds (IX) (A), the product obtained by heating (IX) at 120 °C (B) and that obtained at 150 °C (C).

On the other hand, X, XI, and XII lose all benzene molecules in one step until about 135 °C.

IR Spectra. The infrared absorption spectra of compound IX at several heating steps are shown in Fig. 9. The absorption peaks due to benzene at 1479, 1042, 690, and 672 cm^{-1} disappear upon heating at 120 °C and those due to the NH_3 vibration mode at 1592 and 1089 cm^{-1} disappear upon heating at 150 °C with the shift of $\nu_{C\equiv N}$ at 2150 cm^{-1} to about

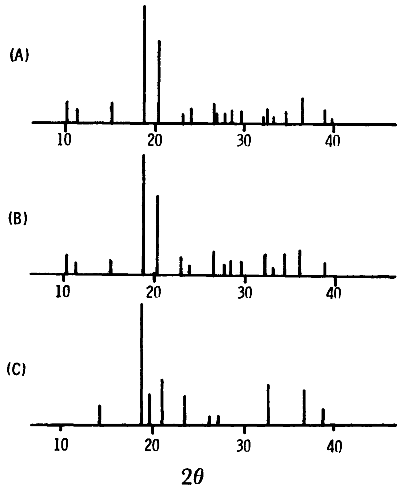

Fig. 10. X-Ray diffraction patterns of compounds (IX) (A), the product obtained by heating (IX) at 120 °C(B) and that obtained at 150 °C(C).

35 cm^{-1} higher.

X-Ray Powder Diffraction Patterns. The X-ray powder diffraction patterns at several heating setps for compound IX are shown in Fig. 10. The pattern obtained by heating at 110 °C where 70% of benzene is removed shows no appreciable change, whereas the one at 150 °C shows a remarkable change. This suggests that the removal of 70% of benzene from the clathrate IX causes no essential change of structure in the host skeleton of the mother clathrate, but the removal of the residual benzene and ammonia gives rise to a structural change. Such a tendency is also observed in compounds X—XII.

Isothermal Kinetics. Isothermal studies were carried out in the same way as those for Hofmann-type clathrates. The enthalpy changes (ΔH) and activation energies (E_a) are given in Table 2.

TABLE 2. ENTHALPY CHANGES ΔH AND ACTIVATION ENERGIES E_a IN THE ELIMINATION OF BENZENE MOLECULE FROM CLATHRATE COMPOUNDS

Compound		ΔH kJ mol^{-1}	E_a kJ mol^{-1}
IX	$Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$	63	76.4
X	$Cd(en)Hg(CN)_4 \cdot 2C_6H_6$	67	74.3
XI	$Cd(en)Cd(CN)_4 \cdot 2C_6H_6$	67	75.6
XII	$Cd(tn)Hg(CN)_4 \cdot 2C_6H_6$	42	65.1

The value of each activation energy is close to that of the corresponding enthalpy change. The activation energy values of Iwamoto-type clathrates are similar to those of Hofmann-type ones, the elimination of benzene proceeding in one step. There are two different kinds of cavities in Iwamoto-type clathrates. However, they cannot be distinguished from each other as regards thermal behavior of the guest molecules. From this point of view, Iwamoto-type clathrates are analogous to Hofmann-type ones with regard to the state of the guest benzene molecules. The activation energy of compound XII gave a somewhat small value. This might be due to the relatively larger repulsion between bulky trimethylenediamine and benzene than that between ethylenediamine and benzene.

References

1) K. A. Hofmann and F. Z. Küspert, *Z. Anorg. Allg. Chem.*, **15**, 204 (1897).

2) E. E. Aynsley, W. A. Campbell, and R. E. Dodd, *Proc. Chem. Soc. (London)*, **1957**, 210.

3) H. M. Powell and J. H. Rayner, *Nature*, **163**, 566 (1949).

4) J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, **1952**, 319.

5) R. Baur and G. Schwarzenbach, *Helv. Chim. Acta*, **43**, 842 (1960).

6) T. Iwamoto, T. Miyoshi, T. Miyamoto, Y. Sasaki, and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, **40**, 1174 (1967).

7) T. Nakano, T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **40**, 1297 (1967).

8) Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **42**, 2412 (1969).

9) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, **7**, 97 (1973).

10) R. Kuroda and Y. Sasaki, *Acta Crystallogr., Sect. B*, **30**, 687 (1974).

11) T. Iwamoto, *Inorg. Chim. Acta*, **2**, 269 (1968).

12) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Nucl. Chem. Lett.*, **6**, 21 (1970).

13) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, **6**, 59 (1972).

14) T. Iwamoto and D. F. Shriver, *Inorg. Chem.*, **11**, 2570 (1972).

15) T. Iwamoto, *Chem. Lett.*, **1973**, 723.

16) R. Kuroda, *Inorg. Nucl. Chem. Lett.*, **9**, 13 (1974).

17) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, **1**, 20 (1967).

18) R. Tsuchiya, Y. Kaji, A. Uehara, and E. Kyuno, *Bull. Chem. Soc. Jpn.*, **42**, 1881 (1969).

19) I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).