# Non-isothermal Studies of Adduct Molecules of Metallic Halides with Oxo Compounds in Solid State. III.

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Non-isothermal studies of some adduct molecules of metallic halides with ethylene glycol dimethyl ether of the type $MX_2(EGDME)_y$ in solid state were carried out with a derivatograph, where M=Mn(II), Co(II), Ni(II), Cu(II) or Cd(II), X=$Cl^-$ or $Br^-$, EGDME=ethylene glycol dimethyl ether and $y$=0.5—1. These adduct molecules lost ethylene glycol dimethyl ether in single or multiple steps upon heating. Thermally stable intermediate products were isolated and characterised by elemental analysis and IR spectral measurement. The activation energy for each step of decomposition of the adduct was evaluated from the analysis of TG, DTG and DTA curves of the respective derivatograms. Enthalpy change was evaluated from the DTA peak area and the order of reaction was found to be unity for each step of decomposition. Thermal parameters for the above adducts were compared with those for the corresponding type of adducts with oxo-compounds like dioxane or tetrahydrofuran.

Works on the adduct molecule with ethylene glycol dimethyl ether were carried out by several groups of workers,[1–11] but they only prepared and characterised some adduct molecules of metallic halides with ethylene glycol dimethyl ether. Ludwig and Schroer[12] carried out thermal decomposition of ethylene glycol dimethyl ether adducts of some metal halides. They investigated the thermal properties of the adducts by thermogravimetry and differential thermal analysis but not by the measurement of DTG, and they did not evaluate the activation energy, order of reaction and enthalpy change for each step of decomposition of the adducts. In continuation of our previous works[13,14] on dioxane and tetrahydrofuran, the present paper deals with thermal decomposition of ethylene glycol dimethyl ether adducts of some metal halides to evaluate the activation energy for decomposition of the adducts from the results by simultaneous TG, DTG, and DTA measurements as well as the order of reaction(n) from the TG curve and $\Delta H$ from the DTA peak area. This paper gives a comparative picture on the thermal properties of adducts similar in composition and a discussion on the thermal properties relating the other oxo-compounds studied earlier.[13,14]

## Experimental

All the adducts were prepared by a method similar to that described previously[13,14] and characterised by elemental analysis and IR spectral measurement. The ethylene glycol dimethyl ether used was sufficiently purified according to the standard procedure.[8]

The following adducts of the metal halides were prepared

1. $MnCl_2 \cdot 0.5EGDME$
2. $MnBr_2 \cdot 1EGDME$
3. $CoCl_2 \cdot 0.5EGDME$
4. $CoBr_2 \cdot 1EGDME$
5. $NiCl_2 \cdot 1EGDME$
6. $NiBr_2 \cdot 1EGDME$
7. $CuCl_2 \cdot 0.5EGDME$
8. $CuBr_2 \cdot 1EGDME$
9. $CdCl_2 \cdot 1EGDME$
10. $CdBr_2 \cdot 1EGDME$

where EGDME represents ethylene glycol dimethyl ether.

A Paulik-Paulik-Erdey type MOM derivatograph was used for thermal analysis. The particle size of the sample was within 150—200 mesh. Heating rate was about 1.5 °C/min. The volume of the sample in each case was the same. Platinum crucible was used. All the experiments were conducted in static air.

## Results

Adducts of $MnBr_2$, $NiBr_2$, $CuBr_2$, $CdCl_2$ and $CdBr_2$ with ethylene glycol dimethyl ether are similar in composition with one another and lose ethylene glycol dimethyl ether in a single step upon heating as indicated by their respective derivatogram in Figs. 1 and 2. A similar single step decomposition is observed in the adduct of $CuCl_2$ although its composition is not similar to that of the former adducts. The adducts of $MnCl_2$ and $CoCl_2$ are similar to one of $CuCl_2$ in composition and they lose ethylene glycol dimethyl ether on heating in different fashion (Fig. 3); *i.e.*, $MCl_2 \cdot 0.5EGDME \rightarrow MCl_2 \cdot 0.25EGDME$; $MCl_2 \cdot 0.25EGDME \rightarrow MCl_2$, where M=Mn(II) or Co(II). The adduct of $NiCl_2$ though it is similar to the adduct of $NiBr_2$ in composition loses ethylene glycol dimethyl ether upon heating in the following way as shown in Fig. 4; $NiCl_2 \cdot 1EGDME \rightarrow NiCl_2 \cdot 0.25EGDME \rightarrow NiCl_2$. The intermediate product *i.e.*, $NiCl_2 \cdot 0.25EGDME$ is not stable. The adduct of $CoBr_2$ which is similar in composition to the major number of adducts described earlier loses ethylene glycol dimethyl ether in multiple steps upon heating as shown in Fig. 4. None of these intermediate products are stable enough to be isolated. Its derivatogram indicates its decomposition in three steps and the intermediate products are very unusual in composition.

The decomposition of all the adducts shows endotherm. Temperature ranges of decomposition and the DTG peak temperatures for the adducts are listed in Table 1. Enthalpy change for each step of decomposition of the adducts was evaluated by the method of Sano[15] using copper sulfate pentahydrate as the standard. When the two DTA curves are too much overlapped with each other, the $\Delta H$ values are evaluated from the overall area of the DTA peaks concerned.

The activation energy for each step of decomposition of the adduct molecules was evaluated (Table 1) from the analysis of the TG curves using Freeman and Carroll's[16] equation. The plots of $\Delta\log(dw/dt)/\Delta\log W_r$ *vs.* $\Delta T^{-1}/\Delta\log W_r \times 10^3$ from TG curves are shown in Fig. 5. The order of reaction for each step of decomposition is found to be unity.

Activation energy for each step of decomposition was also evaluated from the analysis of the DTG curve

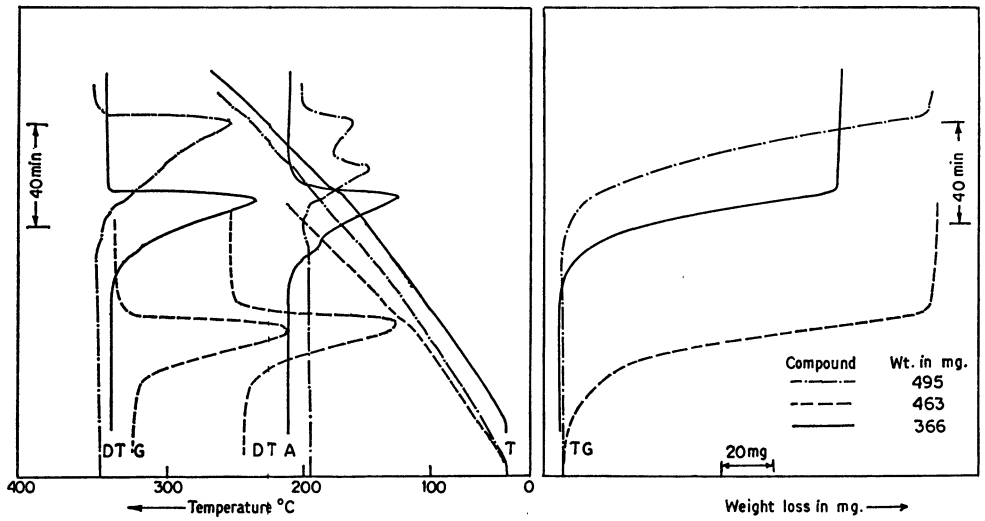


Fig. 1. Derivatograms for $CuBr_2 \cdot 1EGDME$ (-·--·-), $NiBr_2 \cdot 1EGDME$ (----) and $MnBr_2 \cdot 1EGDME$ (——).

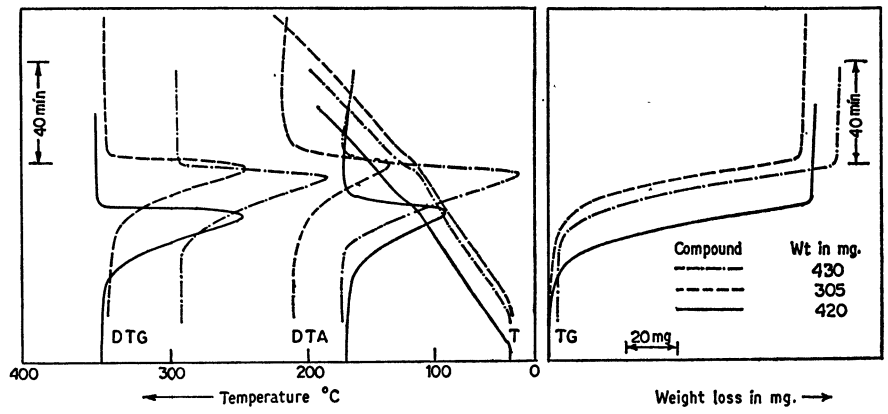


Fig. 2. Derivatograms for $CuCl_2 \cdot 0.5EGDME$ (-·--·-), $CdCl_2 \cdot 1EGDME$ (----) and $CdBr_2 \cdot 1EGDME$ (——).

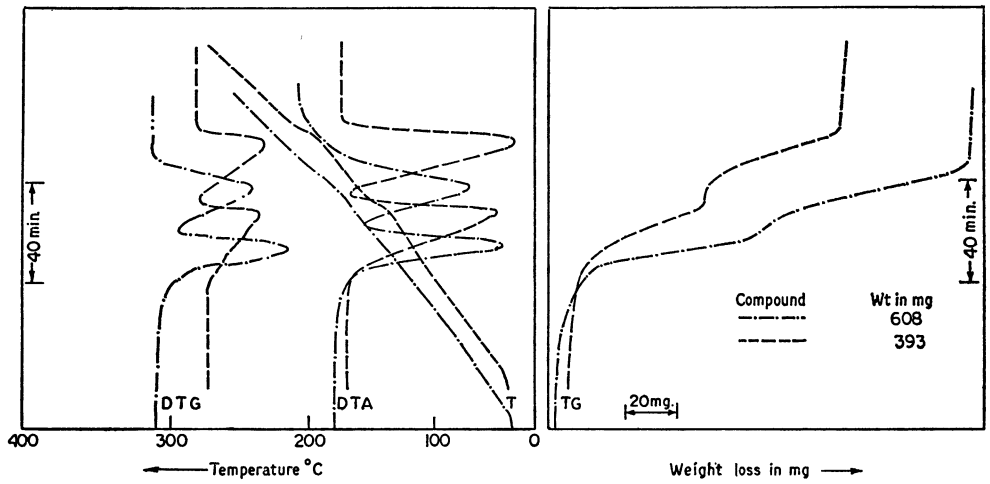


Fig. 3. Derivatograms for $MnCl_2 \cdot 0.5EGDME$ (-·--·-) and $CoCl_2 \cdot 0.5EGDME$ (----).

using the method of Dave and Chopra[17] and the method described in our earlier work[13] and also from the analysis of DTA curve using Brochardt's[18] equation for first order reaction (Table 1). The Arrhenius plots of log $k$ *vs* $T^{-1} \times 10^3$ from DTG and DTA curves are shown in Figs. 6 and 7 respectively.

IR spectra of the adducts were taken to conform the presence of ethylene glycol dimethyl ether molecule in the adduct.

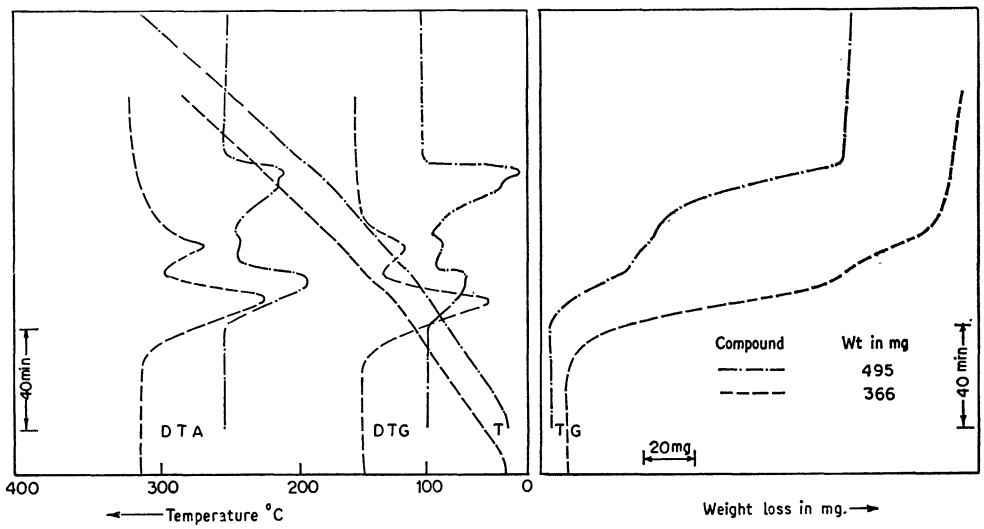


Fig. 4. Derivatograms for $CoBr_2 \cdot 1EGDME$ (-·-·-) and $NiCl_2 \cdot 1EGDME$ (----).

Table 1. Thermal parameters for the decomposition of adduct molecules of some metallic halides with ethylene glycol dimethyl ether

| | Decomposition reaction | Temp. range °C | DTG peak temp. °C | Activation energy $\Delta E_a$ kcal/mol | | | Enthalpy change $\Delta H$ kcal/mol |
|---|---|---|---|---|---|---|---|
| | | | | TG | DTG | DTA | |
| Ia. | $MnCl_2 \cdot 0.5A \rightarrow MnCl_2 \cdot 0.25A$ | 85—140 | 135 | 27.1 | a) | a) | 46.0[b] |
| b. | $MnCl_2 \cdot 0.25A \rightarrow MnCl_2$ | 140—202 | 179 | 49.8 | a) | a) | |
| II. | $MnBr_2 \cdot 1A \rightarrow MnBr_2$ | 107—175 | 169 | 33.5 | 33.5 | 33.5 | 19.5 |
| IIIa. | $CoCl_2 \cdot 0.5A \rightarrow CoCl_2 \cdot 0.25A$ | 100—143 | 135 | 46.0 | 46.0 | 46.0 | 50.0 |
| b. | $CoCl_2 \cdot 0.25A \rightarrow CoCl_2$ | 155—200 | 190 | 46.0 | 41.4 | 46.0 | 57.9 |
| IVa. | $CoBr_2 \cdot 1A \rightarrow CoBr_2 \cdot 0.74A$ | 76—114 | 110 | 46.0 | 46.0 | 39.8 | |
| a'. | $CoBr_2 \cdot 0.74A \rightarrow CoBr_2 \cdot 0.65A$ | 114—144 | 135 | c) | c) | c) | 32.0[b] |
| b. | $CoBr_2 \cdot 0.65A \rightarrow CoBr_2$ | 144—194 | 188 | 46.0 | 39.5 | 39.0 | |
| Va. | $NiCl_2 \cdot 1A \rightarrow NiCl_2 \cdot 0.25A$ | 85—150 | 125 | 32.9 | a) | a) | 26.2[b] |
| b. | $NiCl_2 \cdot 0.25A \rightarrow NiCl_2$ | 150—209 | 167 | 126.5 | a) | a) | |
| VI. | $NiBr_2 \cdot 1A \rightarrow NiBr_2$ | 65—131 | 110 | 23.0 | 29.2 | 29.2 | 28.9 |
| VII. | $CuCl_2 \cdot 0.5A \rightarrow CuCl_2$ | 75—127 | 112 | 33.5 | 33.5 | 33.5 | 33.9 |
| VIII. | $CuBr_2 \cdot 1A \rightarrow CuBr_2$ | 160—245 | 240 | 34.5 | 34.5 | a) | 24.8 |
| IX. | $CdCl_2 \cdot 1A \rightarrow CdCl_2$ | 55—120 | 113 | 23.0 | 27.0 | 27.0 | 22.8 |
| X. | $CdBr_2 \cdot 1A \rightarrow CdBr_2$ | 59—120 | 112 | 23.0 | 23.0 | 23.0 | 22.8 |

A Ethylene glycol dimethyl ether. a) Evaluation of activation energy not possible due to too much overlapping of the corresponding curves. b) Overall enthalpy change. c) Evaluation of activation energy and enthalpy change not possible due to very weak resolution of the curve.

## Discussion

The adduct of $MnCl_2$ was known as $MnCl_2 \cdot 1EGDME$.[8] On repeated preparation we could not isolate an adduct of similar composition. Recently Hengge and Zimmermann[11] isolated the adduct of $MnCl_2$ like ours. Its composition and nature of thermal decomposition are similar to the corresponding adduct with tetrahydrofuran.[14] It is observed that thermal stability of $MnCl_2 \cdot 0.5EGDME$ is greater than the corresponding tetrahydrofuran adduct, whereas its intermediate product, $MnCl_2 \cdot 0.25EGDME$, is thermally less stable than the corresponding tetrahydrofuran adduct. It is also noted that values of activation energies for decomposition of $MnCl_2 \cdot 0.5EGDME \rightarrow MnCl_2 \cdot 0.25EGDME$ and $MnCl_2 \cdot 0.25EGDME \rightarrow MnCl_2$ are less than those for the corresponding tetrahydrofuran adduct.

The adduct of $MnBr_2$ is similar in composition to the corresponding adduct with tetrahydrofuran and dioxane we isolated.[13,14] The thermal stability of $MnBr_2 \cdot 1EGDME$ is higher than the corresponding adduct with tetrahydrofuran and less than the corresponding adduct with dioxane. The value of activation energy evaluated for the decomposition of $MnBr_2 \cdot 1EGDME \rightarrow MnBr_2$ is less than that for the corresponding adduct with dioxane.

The adduct of $CoCl_2$ was isolated as $CoCl_2 \cdot 1EGDME$.[12] Ludwick and Schroer[12] carried out its thermal decomposition and DTA study. In their studies the

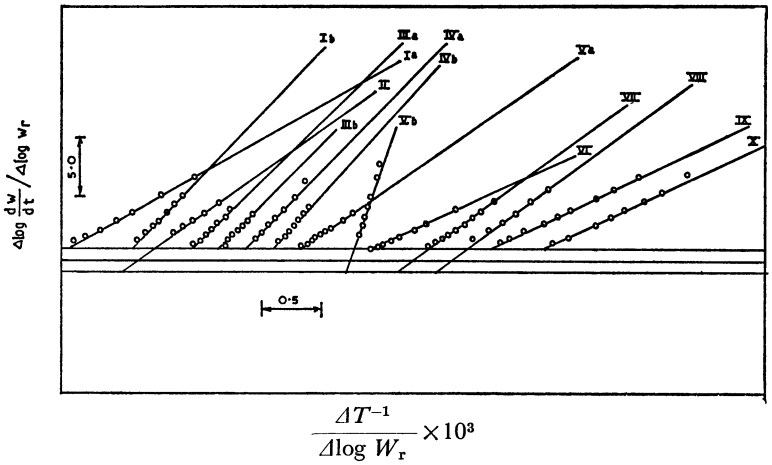


Fig. 5. Plots of $\Delta \log \frac{dw}{dt} / \Delta \log W_r$ *vs.* $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from TG for the decomposition of $MnCl_2 \cdot 0.5$-EGDME → $MnCl_2 \cdot 0.25$EGDME (Ia), $MnCl_2 \cdot 0.25$EGDME → $MnCl_2$ (Ib), $MnBr_2 \cdot 1$EGDME → $MnBr_2$ (II), $CoCl_2 \cdot 0.5$EGDME → $CoCl_2 \cdot 0.25$EGDME (IIIa), $CoCl_2 \cdot 0.25$EGDME → $CoCl_2$ (IIIb), $CoBr_2 \cdot 1$EGDME → $CoBr_2 \cdot 0.74$EGDME (IVa), $CoBr_2 \cdot 0.65$EGDME → $CoBr_2$ (IVb), $NiCl_2 \cdot 1$EGDME → $NiCl_2 \cdot 0.25$EGDME (Va), $NiCl_2 \cdot 0.25$EGDME → $NiCl_2$ (Vb), $NiBr_2 \cdot 1$EGDME → $NiBr_2$ (VI), $CuCl_2 \cdot 0.5$EGDME → $CuCl_2$ (VII), $CuBr_2 \cdot 1$EGDME → $CuBr_2$ (VIII), $CdCl_2 \cdot 1$EGDME → $CdCl_2$ (IX) and $CdBr_2 \cdot 1$EGDME → $CdBr_2$ (X).

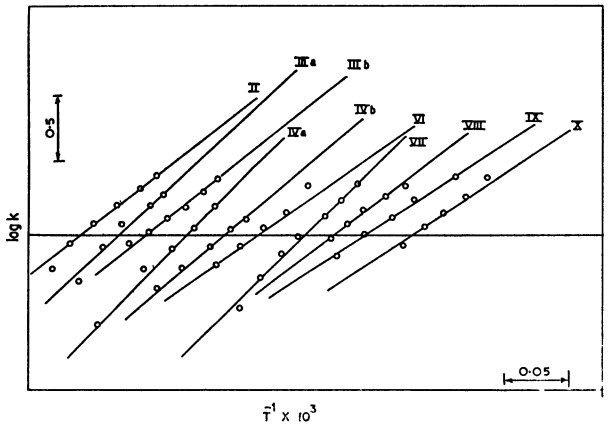


Fig. 6. Arrhenius plots of $\log k$ *vs.* $T^{-1} \times 10^3$, from DTG for the decomposition of $MnBr_2 \cdot 1$EGDME → $MnBr_2$ (II), $CoCl_2 \cdot 0.5$EGDME→$CoCl_2 \cdot 0.25$EGDME (IIIa), CoCl·0.25EGDME → $CoCl_2$ (IIIb), $CoBr_2 \cdot 1$EGDME → $CoBr_2$. 0.74EGDME (IVa), $CoBr_2 \cdot 0.65$EGDME→$CoBr_2$ (IVb), $NiBr_2 \cdot 1$EGDME→$NiBr_2$ (VI), $CuCl_2 \cdot 0.5$ EGDME→$CuCl_2$ (VII), $CuBr_2 \cdot 1$EGDME→$CuBr_2$ (VIII), $CdCl_2 \cdot 1$EGDME→$CdCl_2$ (IX) and $CdBr_2 \cdot 1$EGDME→$CdBr_2$ (X).

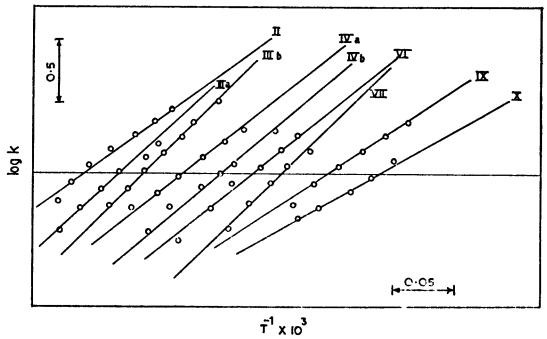


Fig. 7. Arrhenius plots of $\log k$ *vs.* $T^{-1}$, from DTA for the decomposition of $MnBr_2 \cdot 1$EGDME → $MnBr_2$ (II), $CoCl_2 \cdot 0.5$EGDME→$CoCl_2 \cdot 0.25$EGDME (IIIa), $CoCl_2 \cdot 0.25$EGDME→$CoCl_2$ (IIIb), $CoBr_2 \cdot 1$EGDME → $CoBr_2 \cdot 0.74$EGDME (IVa), $CoBr_2 \cdot 0.65$EGDME→ $CoBr_2$ (IVb), $NiBr_2 \cdot 1$EGDME → $NiBr_2$ (VI), $CuCl_2 \cdot 0.5$EGDME→$CuCl_2$ (VII), $CdCl_2 \cdot 1$EGDME→$CdCl_2$ (IX) and $CdBr_2 \cdot 1$EGDME → $CdBr_2$ (X).

existence of $CoCl_2 \cdot 0.5$EGDME was observed from the TG curve and the two overlapped endothermic peaks of the DTA curve. We could not isolate the adduct of the composition described above.[8,12] The adduct $CoCl_2 \cdot 5$EGDME we isolated is similar in composition to that of the adduct with tetrahydrofuran and dioxane, its nature of thermal decomposition being also similar to that of the adduct of $MnCl_2$ and the corresponding adduct with tetrahydrofuran. $CoCl_2 \cdot 0.5$D being similar to the corresponding adduct with ethylene glycol dimethyl ether in composition loses dioxane in a single step. The existence of $CoCl_2 \cdot 0.25$EGDME, $MnCl_2 \cdot 0.25$EGDME and corresponding adduct with THF is indicated by their respective derivatograms. The thermal stability of $CoCl_2 \cdot 0.5$EGDME is equal to the corresponding adduct of $MnCl_2$ and the activation energy for the decomposition of $CoCl_2 \cdot 0.5$EGDME→ $CoCl_2 \cdot 0.25$EGDME is greater than that for the decomposition of $MnCl_2 \cdot 0.5$EGDME→$MnCl_2 \cdot 0.25$-EGDME. On the other hand the thermal stability of $CoCl_2 \cdot 0.25$EGDME is higher than that of the corresponding adduct of $MnCl_2$. However, the thermal stability, activation energy and enthalpy change of this intermediate product are practically equal to that of tetrahydrofuran adduct.[14] The thermal stability of the adduct $CoCl_2 \cdot 0.5$EGDME is lower than the corresponding similar adduct with dioxane but greater than the corresponding tetrahydrofuran adduct. The activation energy for the first step of decomposition of $CoCl_2 \cdot 0.5$EGDME is higher in comparison to the corresponding similar adducts with dioxane and

tetrahydrofuran

The adduct $CoBr_2 \cdot 1EGDME$ we isolated is similar in composition to the adducts isolated by Fowles *et al.*[8] and Ludwig and Schroer.[12] DTA study of $CoBr_2 \cdot 1EGDME$[12] shows that the decomposition takes place in two steps and the intermediate product is very unstable. In our case the nature of decomposition is somewhat different. This is probably due to the very small rate of heating in comparison with that in the earlier work.[12] Though the intermediate products are unstable, we obtained three endothermic peaks in the DTA curve. The weight loss of the second step is very small. Though the composition of the adduct of $CoBr_2$ with ethylene glycol dimethyl ether is similar to that of the corresponding adduct with dioxane, the nature of thermal decomposition of the two differs. The adduct $CoBr_2 \cdot 1D$ loses dioxane in a single step. The thermal stability of $CoBr_2 \cdot 1D$ is lower than that of the corresponding adduct with ethylene glycol dimethyl ether. Activation energy is smaller in case of dioxane adduct.

The composition of the adduct of $NiCl_2$ we isolated differs from that of the corresponding adduct with dioxane and tetrahydrofuran.[13,14]

The adduct of $NiBr_2$ was isolated as $NiBr_2 \cdot 2EGDME$.[12] Its TG and DTA studies indicate multiple steps of decomposition. Ludwig and Schroer could not isolate the adduct as $NiBr_2 \cdot 1EGDME$ thermally. However, Ward[10] isolated the same recently. $NiBr_2 \cdot 1EGDME$ we isolated is similar in composition to the corresponding dioxane adduct[13] but not similar to the corresponding adduct with THF.[14] The nature of thermal decomposition of the adduct $NiBr_2 \cdot 1EGDME$ is similar to the corresponding dioxane adduct, $NiBr_2 \cdot 1D$. With respect to the thermal stability and activation energy of decomposition the ethylene glycol dimethyl ether adduct is less stable than the dioxane adduct in the case of $NiBr_2$.

The adduct $CuCl_2 \cdot 0.5EGDME$ we isolated was reported earlier.[8,12] Although the composition of the adduct of this salt with dioxane and tetrahydrofuran differs from this adduct, the nature of decomposition of this adduct and the adduct of dioxane is the same.

Ethylene glycol dimethyl ether adduct of $CuBr_2$ we isolated is similar in composition to the corresponding adduct with tetrahydrofuran. The dioxane adduct of similar composition is observed as an intermediate during the thermal decomposition of $CuBr_2 \cdot 2D$. Thermal stability and activation energy of $CuBr_2 \cdot 1EGDME$ are equal to those of the corresponding adduct with THF but the adduct $CuBr_2 \cdot 1EGDME$ is thermally more stable than the corresponding dioxane adduct.

Preparation and characterisation of the adduct of $CdCl_2$ and $CdBr_2$ with ethylene glycol dimethyl ether were carried out by Fowles *et al.*[8] We isolated the adducts of $CdCl_2$ and $CdBr_2$ as $CdCl_2 \cdot 1EGDME$ and $CdBr_2 \cdot 1EGDME$ which are similar in composition to their adducts and also similar to the corresponding adduct with tetrahydrofuran but not similar to the corresponding adduct with dioxane in the case of $CdCl_2$. Dioxane forms the adduct of $CdCl_2$ as $CdCl_2 \cdot 0.5D$. The nature of the decomposition of the adducts of both $CdCl_2$ and $CdBr_2$ with ethylene glycol dimethyl ether is similar to the adducts of other oxo-compounds such as tetrahydrofuran and dioxane.[13,14] The thermal stability and activation energy of the decomposition of $CdCl_2 \cdot 1EGDME$ are lower than those of the corresponding tetrahydrofuran adduct. The adduct $CdBr_2 \cdot 1EGDME$ is thermally less stable than the corresponding adduct with dioxane and more stable than that of adduct with tetrahydrofuran. The activation energy of decomposition of ethylene glycol dimethyl ether adduct of $CdBr_2$ is lower than that of the corresponding adduct with tetrahydrofuran or dioxane.

Thermal stability of the adducts of the type $MBr_2 \cdot 1EGDME$, where M=Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) increase in the order: Cu>Mn>Cd>Ni=Co. The thermal stability, activation energy and enthalpy change of decomposition of $CdCl_2 \cdot 1EGDME$ and $CdBr_2 \cdot 1EGDME$ are nearly the same. Such similarities are not observed between the corresponding tetrahydrofuran adducts of $CdCl_2$ and $CdBr_2$.

In general the later step of decomposition gives larger $\Delta H$ value and activation energy than the earlier step. But such a tendency is not observed in the decomposition of all the adducts.

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