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

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Non-isothermal studies of several adduct molecules of metallic halides with oxo-compounds as the type $MX_2(THF)_y$ in solid state were carried out with a Derivatograph, where M is Mn(II), Co(II), Ni(II), Cu(II) or Cd(II), X is Cl^- or Br^-, THF is the abbreviated form of tetrahydrofuran and y is 0.25—2.00. These adduct molecules lost tetrahydrofuran 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 adducts was evaluated from the analysis of TG, DTG, and DTA curves of the respective derivatograms. Enthalpy change was evaluated from DTA peak area and order of reaction was found to be unity for each step of decomposition. Thermal parameters for the above adducts were compared with those of the adducts of dioxane.

The works on the adduct molecules with tetrahydrofuran had been carried out by several workers.[1–13] They only prepared and characterised some adduct molecules of metallic halides with tetrahydrofuran. Rossmanith and Blaha[8,10] studied the thermal decomposition of the adducts of some rare earth bromides. On the other hand, Barnes and Duncan[12] carried out the thermal decomposition of tetrahydrofuran adducts of $CdCl_2$ and $CdBr_2$ with differential scanning calorimeter. They reported the value of enthalpy changes and decomposition temperatures of the adducts. But they did not evaluate the activation energy and order of reaction for the decomposition of the adducts.

In continuation of our previous work on dioxane,[14] the present paper deals with thermal decomposition of tetrahydrofuran adducts of some metallic halides to evaluate the activation energy for decomposition of the adducts from the results by the simultaneous TG, DTG and DTA measurements as well as the order of reaction (n) from TG curve, ΔH from DTA peak area and thermal stability from the first DTG peak temperature. This paper reveals a comparative picture on the thermal properties of the adducts which are similar in composition and also discusses the thermal properties of the adducts with tetrahydrofuran comparing with those of dioxane[14] studied by us.

Experimental

All the adducts were prepared by using the method described in the earlier work[14] and characterised by elemental analysis and IR spectral measurement. The tetrahydrofuran used was sufficiently purified according to the standard procedure.[15]

The following adducts of the metal halides were prepared

1. $MnCl_2 \cdot 0.50$ THF
2. $MnBr_2 \cdot 2.00$ THF
3. $CoCl_2 \cdot 0.50$ THF
4. $NiCl_2 \cdot 0.25$ THF
5. $NiBr_2 \cdot 0.75$ THF
6. $CuCl_2 \cdot 0.70$ THF
7. $CuBr_2 \cdot 1.00$ THF
8. $CdCl_2 \cdot 1.00$ THF
9. $CdBr_2 \cdot 1.00$ THF

where THF represents tetrahydrofuran.

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

Results

The adducts of $CuBr_2$, $CdCl_2$ and $CdBr_2$ have the similar composition to each other and lose one molecule of THF in a single step upon heating as indicated by their respective derivatograms in Fig. 1. While the composition of the adduct of $NiBr_2$ is not similar to that of the above adducts, it loses all molecules of THF in a single step as shown in Fig. 2. Derivatogram of $NiCl_2 \cdot 0.25$ THF in Fig. 3 shows a single step decomposition, whereas its DTA and DTG curves are indicative of double step decomposition. The adducts of $MnCl_2$ and $CoCl_2$ are similar in composition and they lose THF molecule in two steps passing through an intermediate as follows: $MCl_2 \cdot 0.50\ THF \rightarrow MCl_2 \cdot 0.25\ THF$ where M=Mn(II) or Co(II). From the comparison of the TG curve of these two adducts, the range giving a plateau in $MnCl_2 \cdot 0.25$ THF is slightly larger than that of $CoCl_2 \cdot 0.15$ THF. The adduct $CuCl_2 \cdot 0.70$ THF loses oxo-compound in three steps upon heating in the following way as seen in Fig. 2: $CuCl_2 \cdot 0.70\ THF \rightarrow CuCl_2 \cdot 0.50\ THF \rightarrow CuCl_2 \cdot 0.50\ THF/CuCl_2$. The TG curve of $CuCl_2 \cdot 0.70$ THF shows that decomposition of $CuCl_2 \cdot 0.50\ THF \rightarrow CuCl_2 \cdot 0.15$ THF is more rapid than the decomposition of $CuCl_2 \cdot 0.15\ THF \rightarrow CuCl_2$ though both the intermediate products *i.e.*, $CuCl_2 \cdot 0.50$ THF and $CuCl_2 \cdot 0.15$ THF are thermally unstable. The adduct $MnBr_2 \cdot 2.00$ THF loses tetrahydrofuran molecules in three steps as observed in Fig. 3 as follows: $MnBr_2 \cdot 2.00\ THF \rightarrow MnBr_2 \cdot 1.00\ THF \rightarrow MnBr_2 \cdot 0.88\ THF \rightarrow MnBr_2$. The intermediate $MnBr_2 \cdot 1.00$ THF is thermally stable, whereas $MnBr_2 \cdot 0.88$ THF is thermally unstable as observed in its thermogram. However, the existence of $MnBr_2 \cdot 0.88$ THF was verified by repeated analysis.

The decomposition of all the adducts gives endotherm in DTA. Temperature ranges of decomposition and DTG peak temperatures for the adducts are listed in the second and third columns in Table 1 respectively. Enthalpy change for each step of decomposition of the adducts was evaluated by the method of Sano[16] using copper sulfate pentahydrate as the standard and the values are also tabulated in the last column in Table 1. When the two DTA curves are too much overlapped with each other, the ΔH

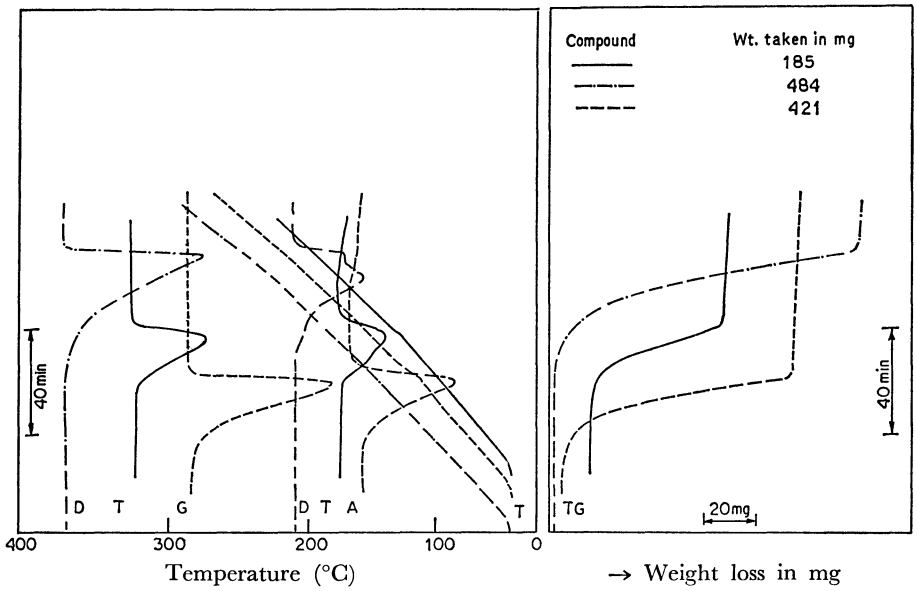

Fig. 1. The derivatograms for $CdCl_2 \cdot 1.00\,THF$ (——), $CuBr_2 \cdot 1.00\,THF$ (—·—) and $CdBr_2 \cdot 1.00\,THF$ (----).

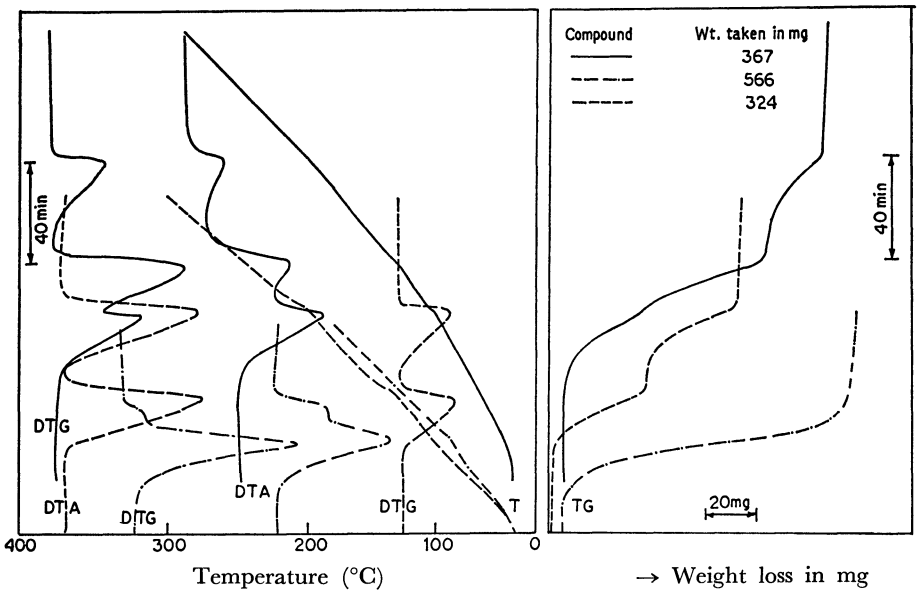

Fig. 2. The derivatograms for $CuCl_2 \cdot 0.70\,THF$ (——), $NiBr_2 \cdot 0.75\,THF$ (—·—) and $MnCl_2 \cdot 0.50\,THF$ (----).

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 from the analysis of the TG curves using Freeman and Carroll's[17] equation. The values are tabulated in the fourth column of Table 1 and the plots of

$$\Delta \log \frac{dw}{dt} \Big/ \Delta \log W_r \text{ vs. } [\Delta T^{-1} / \Delta \log W_r] \times 10^3$$

from TG curves are shown in Fig. 4.

The corresponding values were also evaluated from the analysis of the DTG curve using Dave and Chopra's[18] equation and from the analysis of DTA curve using Brochardt's[19] equation for the first order reaction. These values are tabulated in the fifth and sixth columns in Table 1 respectively. Arrhenius plots of $\log k$ *vs.* $T^{-1} \times 10^3$ from DTG and DTA curves are shown in Figs. 5 and 6 respectively.

IR spectra of the adducts were taken to ensure the presence of tetrahydrofuran molecule in the adduct.

Discussion

The adduct of $MnCl_2$ has been isolated as $MnCl_2 \cdot 1.50\,THF$ by some workers.[5,12] We have failed to isolate $MnCl_2 \cdot 1.50\,THF$. The adduct of this salt with THF we isolated differs in composition from the corresponding adduct with dioxane (D) studied by us. The dioxane adduct of this salt lost oxo compounds in a single step upon heating, whereas $MnCl_2 \cdot 0.50$ THF loses tetrahydrofuran in double step passing

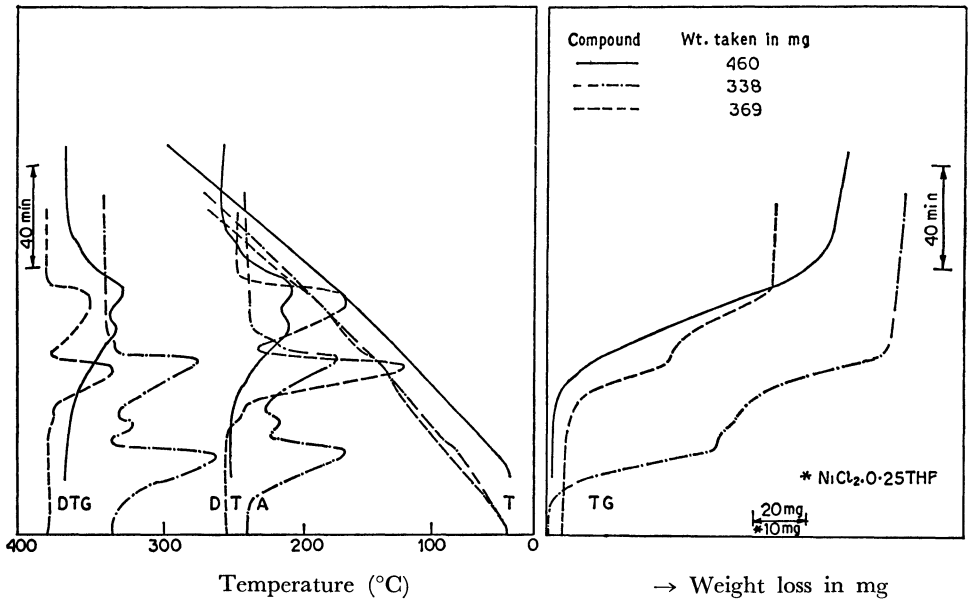

Fig. 3. The derivatograms for $NiCl_2 \cdot 0.25$ THF (——), $MnBr_2 \cdot 2.00$ THF (—·—) and $CoCl_2 \cdot 0.50$ THF (----).

Table 1. Thermal parameters for the decomposition of adduct molecules of some metallic halides with tetrahydrofuran

	Decomposition reactions	Temp. range °C	DTG peak temp. °C	Activation energy E_a kcal/mol of THF			Enthalpy change ΔH kcal/mol of THF
				TG	DTG	DTA	
Ia.	$MnCl_2 \cdot 0.50L \rightarrow MnCl_2 \cdot 0.25L$	88—135	125	41.4	39.0	41.4	61.5
b.	$MnCl_2 \cdot 0.25L \rightarrow MnCl_2$	157—205	195	72.2	71.5	71.5	58.6
IIa.	$MnBr_2 \cdot 2.00L \rightarrow MnBr_2 \cdot 1.00L$	41— 80	73	30.7	30.7	30.7	18.2
a'.	$MnBr_2 \cdot 1.00L \rightarrow MnBr_2 \cdot 0.88L$	95—108	100	b)	b)	b)	b)
b.	$MnBr_2 \cdot 0.88L \rightarrow MnBr_2$	108—148	140	55.2	55.2	55.2	22.5
IIIa.	$CoCl_2 \cdot 0.50L \rightarrow CoCl_2 \cdot 0.25L$	100—145	127	41.8	37.6	37.6	62.5
b.	$CoCl_2 \cdot 0.25L \rightarrow CoCl_2$	145—205	192	46.0	46.0	46.0	57.7
IV.	$NiCl_2 \cdot 0.25L \rightarrow NiCl_2$	78—234	145	30.7	b)	b)	45.0[a]
V.	$NiBr_2 \cdot 0.75L \rightarrow NiBr_2$	40—126	88	19.7	b)	b)	19.1
VIa.	$CuCl_2 \cdot 0.70L \rightarrow CuCl_2 \cdot 0.50L$	63— 98	94	38.9	b)	b)	38.8[a]
b.	$CuCl_2 \cdot 0.50L \rightarrow CuCl_2 \cdot 0.15L$	98—135	128	44.2	b)	b)	
c.	$CuCl_2 \cdot 0.15L \rightarrow CuCl_2$	135—200	197	36.0	36.0	36.0	24.1
VII.	$CuBr_2 \cdot 1.00L \rightarrow CuBr_2$	155—250	244	34.5	35.5	b)	14.7
VIII.	$CdCl_2 \cdot 1.00L \rightarrow CdCl_2$	80—135	125	31.2	32.9	29.6	12.7 (10.4 ± 0.2)[c]
IX.	$CdBr_2 \cdot 1.00L \rightarrow CdBr_2$	36—116	108	28.8	33.4	33.4	15.4 (15.1 ± 0.4)[c]

L: Represents tetrahydrofuran. a) Indicates overall enthalpy change. b) Evaluation of activation energy was not possible due to overlapping of the corresponding curves. c) Value in the parentheses evaluated by Barnes and Duncan.

through a thermally stable intermediate $MnCl_2 \cdot 0.25$ THF. The thermal stability of $MnCl_2 \cdot 1.00$ D is greater than that of $MnCl_2 \cdot 0.50$ THF but smaller than that of $MnCl_2 \cdot 0.25$ THF. The value of activation energy and enthalpy change for the decomposition of both the steps of this adduct are high in comparison with that of the adduct with dioxane.

The composition of the adducts $MnBr_2 \cdot 2.00$ THF is similar to the corresponding adduct with dioxane but their nature of decomposition differs from each other. Dioxane adduct of the salt lost oxo compound in two steps passing through a thermally stable intermediate $MnBr_2 \cdot 1.00$ D. Whereas, the corresponding tetrahydrofuran adduct loses oxo compound in three steps passing through a stable intermediate $MnBr_2 \cdot 1.00$ THF like dioxane and then through an unstable intermediate $MnBr_2 \cdot 0.88$ THF. The thermal stability of $MnBr_2 \cdot 2.00$ THF is low in comparison with that of the corresponding adduct with dioxane. The activation energy for the first step of decomposition of the adduct with tetrahydrofuran is also low in comparison with that of the dioxane but the value of enthalpy of this adduct is high in comparison with that of the adduct with dioxane. The thermal stability of the

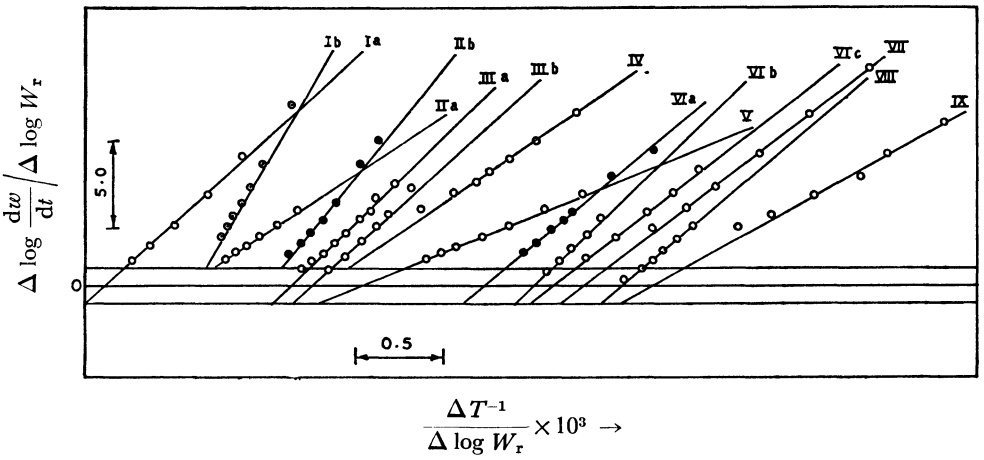

Fig. 4. Plots of $\Delta \log \frac{dw}{dt} / \Delta \log W_r$ *vs.* $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from TG for the decomposition of $MnCl_2 \cdot 0.50$ THF→$MnCl_2 \cdot 0.25$ THF (Ia), $MnCl_2 \cdot 0.25$ THF→$MnCl_2$ (Ib), $MnBr_2 \cdot 2.00$ THF→$MnBr_2 \cdot 1.00$ THF (IIa), $MnBr_2 \cdot 0.88$ THF→$MnBr_2$ (IIb), $CoCl_2 \cdot 0.50$ THF→$CoCl_2 \cdot 0.25$ THF (IIIa), $CoCl_2 \cdot 0.25$ THF→$CoCl_2$ (IIIb), $NiCl_2 \cdot 0.25$ THF→$NiCl_2$ (IV), $NiBr_2 \cdot 0.75$ THF→$NiBr_2$ (V), $CuCl_2 \cdot 0.70$ THF→$CuCl_2 \cdot 0.50$ THF (VIa), $CuCl_2 \cdot 0.50$ THF→$CuCl_2 \cdot 0.15$ THF (VIb), $CuCl_2 \cdot 0.15$ THF→$CuCl_2$ (VIc), $CuBr_2 \cdot 1.00$ THF→$CuBr_2$ (VII), $CdCl_2 \cdot 1.00$ THF→$CdCl_2$ (VIII) and $CdBr_2 \cdot 1.00$ THF→$CdBr_2$ (IX).

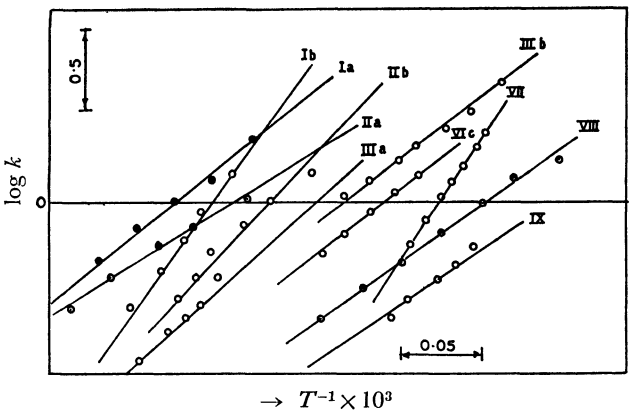

Fig. 5. Arrhenius plots of $\log k$ *vs.* $T^{-1} \times 10^3$, from DTG for the decomposition of $MnCl_2 \cdot 0.50$ THF→$MnCl_2 \cdot 0.25$ THF (Ia), $MnCl_2 \cdot 0.25$ THF→$MnCl_2$ (Ib), $MnBr_2 \cdot 2.00$ THF→$MnBr_2 \cdot 1.00$ THF (IIa), $MnBr_2 \cdot 0.88$ THF→$MnBr_2$ (IIb), $CoCl_2 \cdot 0.50$ THF→$CoCl_2 \cdot 0.25$ THF (IIIa), $CoCl_2 \cdot 0.25$ THF→$CoCl_2$ (IIIb), $CuCl_2 \cdot 0.15$ THF→$CuCl_2$ (VIc), $CuBr_2 \cdot 1.00$ THF→$CuBr_2$ (VII), $CdCl_2 \cdot 1.00$ THF→$CdCl_2$ (VIII) and $CdBr_2 \cdot 1.00$ THF→$CdBr_2$ (IX).

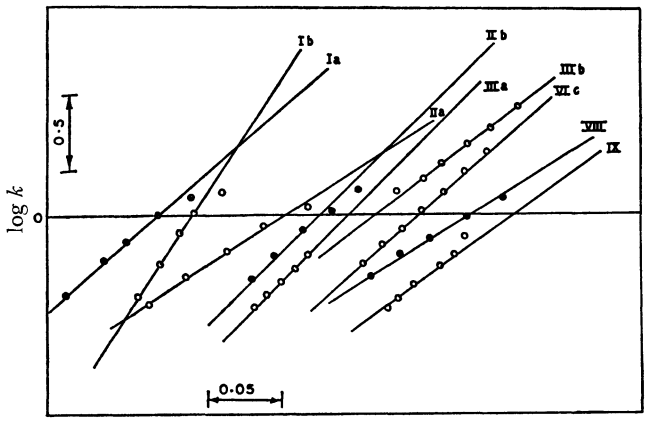

Fig. 6. Arrhenius plots of $\log k$ *vs.* $T^{-1} \times 10^3$, from DTA for the decomposition of $MnCl_2 \cdot 0.50$ THF→$MnCl_2 \cdot 0.25$ THF (Ia), $MnCl_2 \cdot 0.25$ THF→$MnCl_2$ (Ib), $MnBr_2 \cdot 2.00$ THF→$MnBr_2 \cdot 1.00$ THF (IIa), $MnBr_2 \cdot 0.88$ THF→$MnBr_2$ (IIb), $CoCl_2 \cdot 0.50$ THF→$CoCl_2 \cdot 0.25$ THF (IIIa), $CoCl_2 \cdot 0.25$ THF→$CoCl_2$ (IIIb), $CuCl_2 \cdot 0.15$ THF→$CuCl_2$ (VIc), $CdCl_2 \cdot 1.00$ THF→$CdCl_2$ (VIII) and $CdBr_2 \cdot 1.00$ THF→$CdBr_2$ (IX).

intermediate $MnBr_2 \cdot 1.00$ THF is also low in comparison with $MnBr_2 \cdot 1.00$ D.

The adducts of $CoCl_2$ with tetrahydrofuran isolated by Kern[5] and also by Fowles *et al.*[13] were similar in composition *i.e.*, $CoCl_2 \cdot 1.50$ THF. We isolated the adduct of the same salt with tetrahydrofuran as $CoCl_2 \cdot 0.50$ THF which is similar in composition to the adduct with dioxane isolated by us. The composition and the nature of decomposition of $CoCl_2 \cdot 0.50$ THF are similar to the adduct of $MnCl_2$ with this oxo compound. Both undergo decomposition through an intermediate $MCl_2 \cdot 0.25$ THF, where M=Co or Mn. Although the adduct of the same salt with dioxane is similar in composition, it eliminated oxo compound in single step. The values of activation energy and enthalpy change for the decomposition of $CoCl_2 \cdot 0.50$ THF→$CoCl_2 \cdot 0.25$ THF are slightly low in comparison with that of the decomposition $MnCl_2 \cdot 0.50$ THF→$MnCl_2 \cdot 0.25$ THF. The activation energy for the decomposition of $CoCl_2 \cdot 0.25$ THF→$CoCl_2$ is very low in comparison with that for the corresponding step of decomposition of adduct of $MnCl_2$ with THF, whereas the value of enthalpy change for the decomposition of $CoCl_2 \cdot 0.25$ THF is slightly higher than the corresponding adduct of $MnCl_2$ with dioxane. It is observed that the activation energy and enthalpy change for the decomposition of $CoCl_2 \cdot 0.50$ D→$CoCl_2$ is low in comparison with those for the decomposition of the corresponding adduct of $CoCl_2$ with THF though

$CoCl_2 \cdot 0.50$ D decomposes at a temperature higher than that of $CoCl_2 \cdot 0.50$ THF. This may be due to the fact that the adducts differ from each other in the nature of decomposition.

Kern[5] isolated the adduct of $NiCl_2$ as $NiCl_2 \cdot 2.00$ THF by starting from $NiCl_2 \cdot CH_3CN$ complex. Whereas we isolated the adduct as $NiCl_2 \cdot 0.25$ THF alone by starting from anhydrous nickel chloride. The composition of this adduct is similar to that of the intermediate product of the adducts of $MnCl_2$ and $CoCl_2$ with this oxo compound but differs from the adduct of the same salt with dioxane. The thermal stability and the values of activation energy and enthalpy change of decomposition of $NiCl_2 \cdot 0.25$ THF are lower than those of the decomposition of $MnCl_2 \cdot 0.25$ THF$\rightarrow MnCl_2$ and $CoCl_2 \cdot 0.25$ THF$\rightarrow CoCl_2$. Whereas the value of activation energy of decomposition of $NiCl_2 \cdot 1.50$ D$\rightarrow NiCl_2$ is close to the value obtained for the decomposition of $NiCl_2 \cdot 0.25$ THF though the value of enthalpy change for the decomposition of the latter is higher than that of the former.

We isolated the adduct of $NiBr_2$ with this present oxo-compound as $NiBr_2 \cdot 0.75$ THF, but the adduct of dioxane we isolated was simple in composition, though single step of decomposition is observed in both the adducts. This adduct molecule is thermally less stable than the adduct with dioxane. The value of activation energy of this adduct is also lower than that of the adduct with dioxane. Whereas, enthalpy change of $NiBr_2 \cdot 0.70$ THF is higher than that of the adduct with dioxane.

The adduct of $CuCl_2$ with THF was reported earlier by Kern[5] as $CuCl_2 \cdot 0.80$ THF. We isolated the adduct of $CuCl_2$ as $CuCl_2 \cdot 0.70$ THF. The dioxane adduct of $CuCl_2$ was reported earlier by us[14] as $CuCl_2 \cdot 0.75$ D which lost oxo compound in single step, whereas the adduct $CuCl_2 \cdot 0.70$ THF loses oxo compounds in three steps. The thermal stability of the adduct $CuCl_2 \cdot 0.70$ THF is lower than that of the adduct with dioxane we isolated. Whereas, the value of activation energy of this adduct is higher than that of the adduct with dioxane. The intermediate product $CuCl_2 \cdot 0.50$ THF shows similarity in composition with the adduct of $MnCl_2$ and $CoCl_2$ with this oxo compound. The thermally unstable $CuCl_2 \cdot 0.50$ THF decomposes through an intermediate $CuCl_2 \cdot 0.15$ THF which differs in composition from the intermediate product of the adduct of $MnCl_2$ and $CoCl_2$ with THF.

The composition of the adduct of $CuBr_2$ with THF is not similar to that of the adduct of the same salt with dioxane and $CuBr_2 \cdot 1.00$ D as an intermediate product of $CuBr_2 \cdot 2.00$ D corresponds to the adduct with this oxo compound isolated by us. The adduct $CuBr_2 \cdot 1.00$ THF decomposes at higher temperature than that of adduct with dioxane. The activation energy for the decomposition of this adduct is slightly lower than that of the adduct with dioxane but the corresponding enthalpy change is high in comparison with that of the dioxane adduct.

The adduct $CdCl_2 \cdot 1.00$ THF isolated by us is similar in composition to the adduct reported earlier.[12] The composition of dioxane adduct of $CdCl_2$ differs from the adduct of the same salt with tetrahydrofuran but both the adducts lose their oxo compounds in a single step upon heating. The thermal stability, activation energy and enthalpy change for decomposition of this tetrahydrofuran adduct is lower than those of the adduct with dioxane. Barnes and Duncan[12] investigated the thermal decomposition of $CdCl_2 \cdot 1.00$ THF with differential scanning calorimeter, where the heating rate was 8 °C/min. The initial decomposition temperature and peak temperature for this adduct reported by them were 105 and 147 °C respectively. Whereas we observe 80 and 125 °C as the initial decomposition temperature and peak temperature respectively, though the value of enthalpy change evaluated by us is very close to the value reported by them.

The tetrahydrofuran adduct of $CdBr_2$ reported earlier[12] is same in composition to the adduct isolated by us and also similar in composition to the corresponding adduct of dioxane.[14] Both the adducts lose their oxo compounds in a single step. This tetrahydrofuran adduct is thermally less stable than the corresponding dioxane adduct. Whereas, the values of activation energy and enthalpy change for the decomposition of adduct with tetrahydrofuran are very close to that of dioxane. Barnes and Duncan[12] also carried out the thermal decomposition of $CdBr_2 \cdot 1.00$ THF and reported 62 and 177 °C as initial and maximum decomposition temperatures respectively, whereas in our cases these temperatures are 36 and 108 °C respectively. But the value of enthalpy change evaluated by them is very close to the value reported by us.

Thermal stability of the adducts of the composition $MBr_2 \cdot 1.00$ THF where M=Mn(II), Cu(II) and Cd(II) owing to the difference of DTG peak temperature increases in the order Mn<Cd<Cu. The values of activation energy for the decomposition of the adducts of $CuBr_2$ and $CdBr_2$ are close. The values of enthalpy change for these two adducts are also same. Thermal stability of the adduct of $CdCl_2$ is higher than that of the corresponding bromide adduct. Whereas, the value of enthalpy change is higher in the case of bromide adduct than that of chloride, though the values of activation energy of both are close. The general comparative review shows that thermal stability of the adducts of dioxane is higher than the corresponding tetrahydrofuran adducts with a few exception in $CuBr_2 \cdot 1.00$ THF and the corresponding dioxane adduct.

The difference of the values of activation energy for the decomposition of adducts evaluated from TG, DTG and DTA curves is not too much. This shows that all the methods used for the evaluation of activation energy are standard. In general, the value of activation energy for the latter step of decomposition gives larger value than the former. This phenomenon is observed in the decomposition of adducts with tetrahydrofuran like the adducts with dioxane. However, there is exception in the value of activation energies for the first and second step of decompositions of $CuCl_2 \cdot 0.70$ THF like the values obtained for the second and third step of decomposition of $CoBr_2 \cdot 2.00$ D reported by us.

It is noticed that the value of enthalpy change for the decomposition of the adduct is related with the

composition of the adducts; it shows low value where the composition of the adduct is simple, *i.e.*, 12.7 kcal/mol for $CdCl_2 \cdot 1.00$ THF and high value where the composition of the adduct is not so simple, *i.e.*, 63.5 kcal/mol for $CoCl_2 \cdot 0.50$ THF. In general the latter decomposition gives larger ΔH value than the former one. But such tendencies are not observed in the decomposition of all the adducts.

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