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NON-ISOTHERMAL STUDIES OF ADDUCT MOLECULES OF METALLIC HALIDES WITH OXO-COMPOUNDS IN SOLID STATE. V

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ABSTRACT

Non-isothermal studies of some adduct molecules of metallic halides with tetrahydropyran as the type $MX_2(THP)_y$ 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^-, THP = tetrahydropyran and $y = 0.1$–1. These adduct molecules lost tetrahydropyran 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 derivatogram. The 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 the adducts of other oxo-compounds like dioxan, tetrahydrofuran, ethylene glycol dimethyl ether and di-isopropyl ether.

INTRODUCTION

The works on the adduct molecules of tetrahydropyran have been carried out by several groups of workers[1–7]. They only prepared and characterised some adduct molecules of metallic halides with this oxo-compound. We reported earlier, non-isothermal studies of adduct molecules of metallic halides with oxo-compounds like dioxan (D)[8], tetrahydrofuran (THF)[9], ethylene glycol dimethyl ether (EGDME)[10] and di-isopropyl ether (DIPE)[11]. In continuation to these works this paper deals with the thermal decomposition of tetrahydropyran adducts of some metal halides to evaluate the activation energy of decomposition by simultaneous TG, DTG and DTA measurements as well as the order of reaction (n) from the TG curve and ΔH from the DTA peak area. In addition to the evaluation of these thermal parameters, this paper reveals a comparative picture on the thermal properties of decomposition of adducts of metallic halides relating the other oxo-compounds studied by us[8–11].

EXPERIMENTAL

All the adducts were prepared by the method described in our earlier work[8] and characterised by elemental analysis and IR spectral measurement. Tetrahydropyran used was sufficiently purified and dried according to the standard procedure[12].

The following adducts of metal halides were prepared: 1. $MnCl_2\cdot0.50THP$; 2. $MnBr_2\cdot0.75THP$; 3. $CoCl_2\cdot0.50THP$; 4. $CoBr_2\cdot1.00THP$; 5. $NiCl_2\cdot0.20THP$; 6. $NiBr_2\cdot0.10THP$; 7. $CuCl_2\cdot0.50THP$; 8. $CuBr_2\cdot1.00THP$; 9. $CdCl_2\cdot0.75THP$; 10. $CdCl_2\cdot0.20THP$; 11. $CdBr_2\cdot1.00THP$, where THP represents tetrahydropyran.

A Paulik–Paulik–Erdey type MOM derivatograph was used for thermal analysis. A platinum crucible was used and the heating rate was about 1.5 °C min^{-1}. The particle size of the sample was within 150–200 mesh. The volume of the sample in each case was the same. All these experiments were conducted in static air.

RESULTS

The adducts of $MnCl_2$ and $CoCl_2$ with tetrahydropyran are similar in composition and lose oxo-compounds in two steps (Fig. 1) via an intermediate $MCl_2\cdot0.25THP$ where M = Mn(II) or Co(II), though $CoCl_2\cdot0.25THP$ is not so thermally stable like the $MnCl_2$ compound. Figure 1 shows the derivatogram of the adduct $MnBr_2\cdot0.75THP$ which loses tetrahydropyran passing through a thermally unstable intermediate $MnBr_2\cdot0.60THP$. Whereas, the adducts of $NiCl_2$, $NiBr_2$, $CuCl_2$, $CdCl_2$ and $CdBr_2$ lose the oxo-compound in single step observed from the derivatograms (Figs. 2–4), although these adducts differ in composition from each other

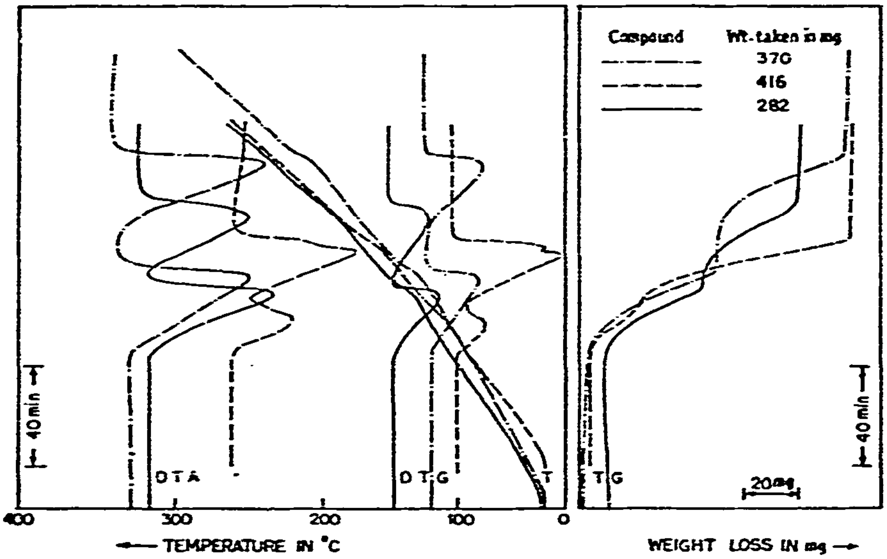

Fig. 1. Derivatograms for the decomposition of $MnCl_2\cdot0.50THP$ (—·—·—), $MnBr_2\cdot0.75THP$ (– – –) and $CoCl_2\cdot0.50THP$ (———).

except the adducts of $NiCl_2$ and $CdCl_2$. The adducts of $CoBr_2$ and $CuBr_2$ are similar in composition and lose the oxo-compound in three steps upon heating. But none of the intermediates are thermally stable and also none of the compositions of the intermediates of these two adducts are similar as observed from the respective derivatogram shown in Figs. 2 and 3.

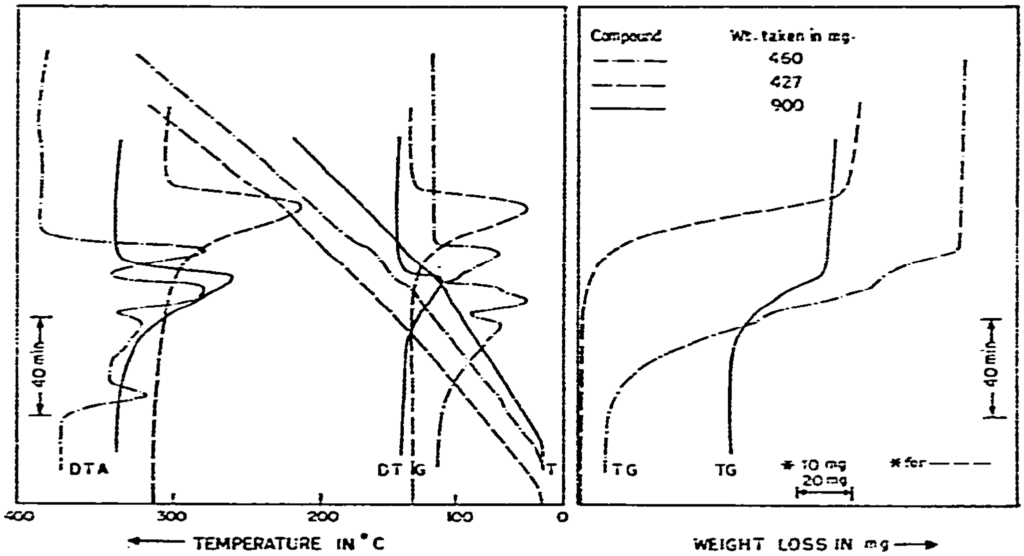

Fig. 2. Derivatograms for the decomposition of $CoBr_2 \cdot 1.00THP$ (—·—·—), $NiCl_2 \cdot 0.20THP$ (— — —) and $NiBr_2 \cdot 0.10THP$ (———).

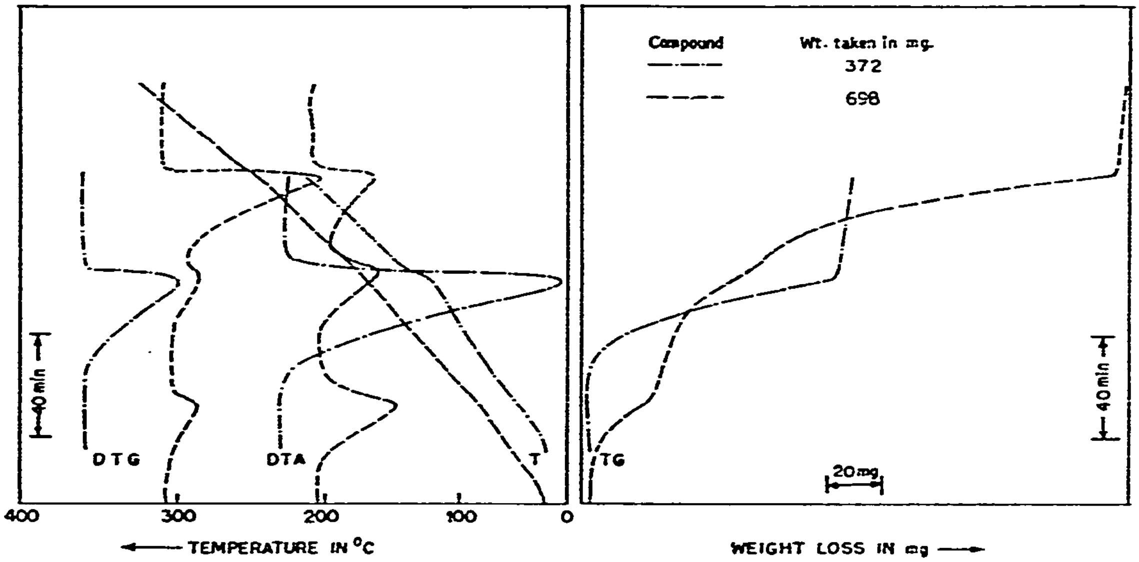

Fig. 3. Derivatograms for the decomposition of $CuCl_2 \cdot 0.50THP$ (—·—·—) and $CuBr_2 \cdot 1.00THP$ (— — —).

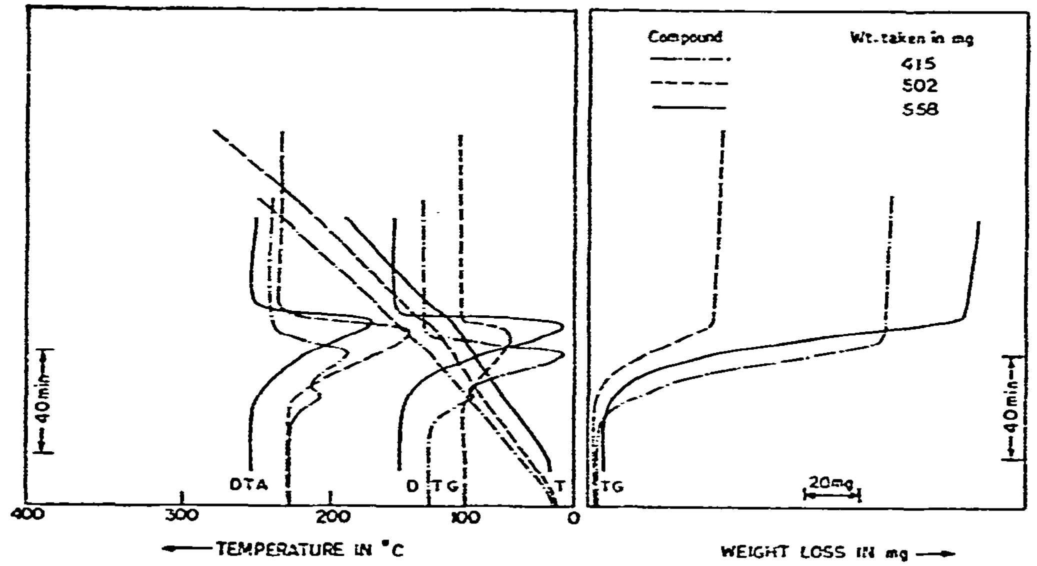

Fig. 4. Derivatograms for the decomposition of $CdCl_2 \cdot 0.75THP$ (—.—.—), $CdCl_2 0.20THP$ (– – –) and $CdBr_2 \cdot 1.00THP$ (———).

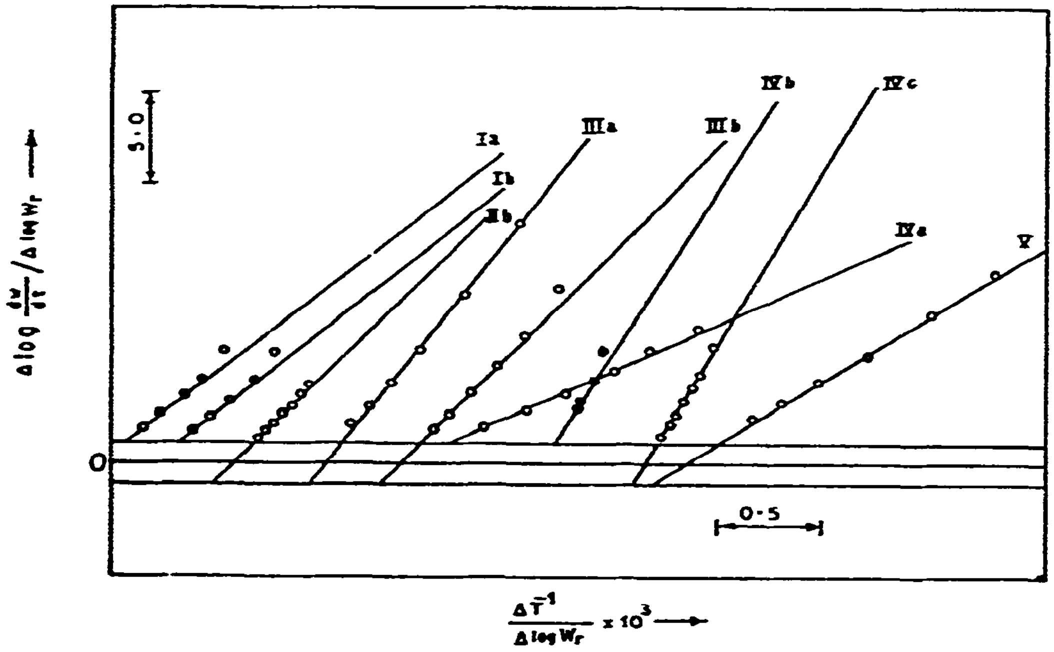

Fig. 5. Plots of $\Delta \log (dw/dt)/\Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from the TG curves for the decomposition of $MnCl_2 \cdot 0.50THP \rightarrow MnCl_2 \cdot 0.25THP$(Ia), $MnCl_2 \cdot 0.25THP \rightarrow MnCl_2$(Ib), $MnBr_2 \cdot 0.60THP \rightarrow MnBr_2$(IIb) $CoCl_2 \cdot 0.50THP \rightarrow CoCl_2 \cdot 0.25THP$(IIIa), $CoCl_2 \cdot 0.25THP \rightarrow CoCl_2$(IIIb), $CoBr_2 \cdot 1.00THP \rightarrow CoBr_2 \cdot 0.55THP$(IVa), $CoBr_2 \cdot 0.55THP \rightarrow CoBr_2 \cdot 0.25THP$(IVb), $CoBr_2 \cdot 0.25THP \rightarrow CoBr_2$(IVc) and $NiCl_2 \cdot 0.20THP \rightarrow NiCl_2$(V).

TABLE 1

THERMAL PARAMETERS FOR THE DECOMPOSITION OF ADDUCT MOLECULES OF SOME METALLIC HALIDES WITH TETRAHYDROPYRAN

Decomposition reaction	*Temp. range (°C)*	*DTG peak temp. (°C)*	*Activation energy (kcal mol^{-1})*			*Enthalpy change (kcal mol^{-1})*
			TG	*DTG*	*DTA*	
(Ia) $MnCl_2 \cdot 0.50L \rightarrow MnCl_2 \cdot 0.25L$	89–134	129	35.8	35.8	33.0	66.3
(Ib) $MnCl_2 \cdot 0.25L \rightarrow MnCl_2$	156–214	205	40.3	40.3	40.3	64.9
(IIa) $MnBr_2 \cdot 0.75L \rightarrow MnBr_2 \cdot 0.60L$	88–125	110	—	—	36.8	36.9
(IIb) $MnBr_2 \cdot 0.60L \rightarrow MnBr_2$	125–170	155	50.6	—	50.6	23.5
(IIIa) $CoCl_2 \cdot 0.50L \rightarrow CoCl_2 \cdot 0.25L$	100–145	135	58.5	50.6	50.6	65.2
(IIIb) $CoCl_2 \cdot 0.25L \rightarrow CoCl_2$	145–205	190	50.6	46.0	50.6	65.2
(IVa) $CoBr_2 \cdot 1.00L \rightarrow CoBr_2 \cdot 0.55L$	50–118	110	23.0	—	—	
(IVb) $CoBr_2 \cdot 0.55L \rightarrow CoBr_2 \cdot 0.25L$	118–139	127	76.6	—	—	61.3[a]
(IVc) $CoBr_2 \cdot 0.25L \rightarrow CoBr_2$	139–169	160	82.8	—	—	
(V) $NiCl_2 \cdot 0.20L \rightarrow NiCl_2$	143–267	225	30.6	51.8	51.8	69.5
(VI) $NiBr_2 \cdot 0.10L \rightarrow NiBr_2$	70–120	112	41.4	41.4	41.4	84.2
(VII) $CuCl_2 \cdot 0.50L \rightarrow CuCl_2$	75–129	119	30.7	30.7	30.7	84.6
(VIIIa) $CuBr_2 \cdot 1.00L \rightarrow CuBr_2 \cdot 0.88L$	43–95	83	30.6	28.8	28.8	73.3
(VIIIb) $CuBr_2 \cdot 0.88L \rightarrow CuBr_2 \cdot 0.68L$	95–185	173	35.8	—	35.8	29.9
(VIIIc) $CuBr_2 \cdot 0.68L \rightarrow CuBr_2$	185–250	245	37.0	—	46.0	7.8
(IX) $CdCl_2 \cdot 0.75L \rightarrow CdCl_2$	65–142	125	26.3	—	—	15.2
(X) $CdCl_2 \cdot 0.20L \rightarrow CdCl_2$	75–131	127	46.0	46.0	46.0	68.0
(XI) $CdBr_2 \cdot 1.00L \rightarrow CdBr_2$	55–117	108	23.0	38.0	38.0	19.5

L denotes tetrahydropyran.

[a] These indicate the overall enthalpy changes where DTA curves overlap too much.

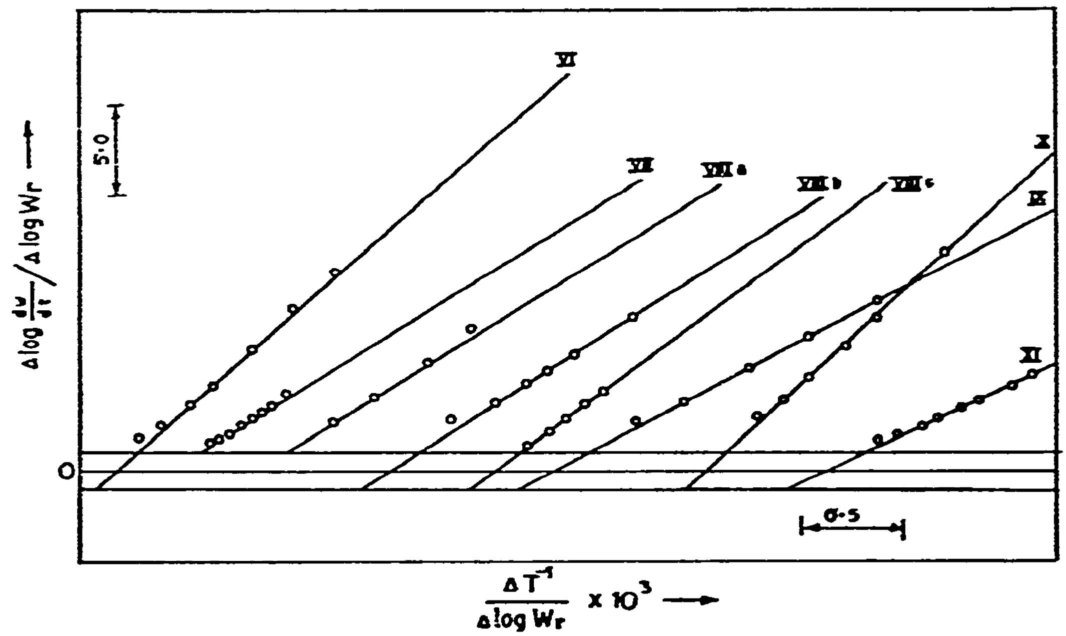

Fig. 6. Plots of Δ log (dw/dt)/Δ log W_r vs. ΔT^{-1}/Δ log W_r × 10^3 from the TG curves for the decomposition of $NiBr_2 \cdot 0.10THP$ → $NiBr_2$(VI), $CuCl_2 \cdot 0.50THP$ → $CuCl_2$(VII), $CuBr_2 \cdot 1.00THP$ → $CuBr_2 \cdot 0.88THP$(VIIIa), $CuBr_2 \cdot 0.88THP$ → $CuBr_2 \cdot 0.68THP$(VIIIb), $CuBr_2 \cdot 0.68THP$ → $CuBr_2$(VIIIc), $CdCl_2 \cdot 0.75THP$ → $CdCl_2$(IX), $CdCl_2 \cdot 0.20THP$ → $CdCl_2$(X) and $CdBr_2 \cdot 1.00THP$ → $CdBr_2$(XI).

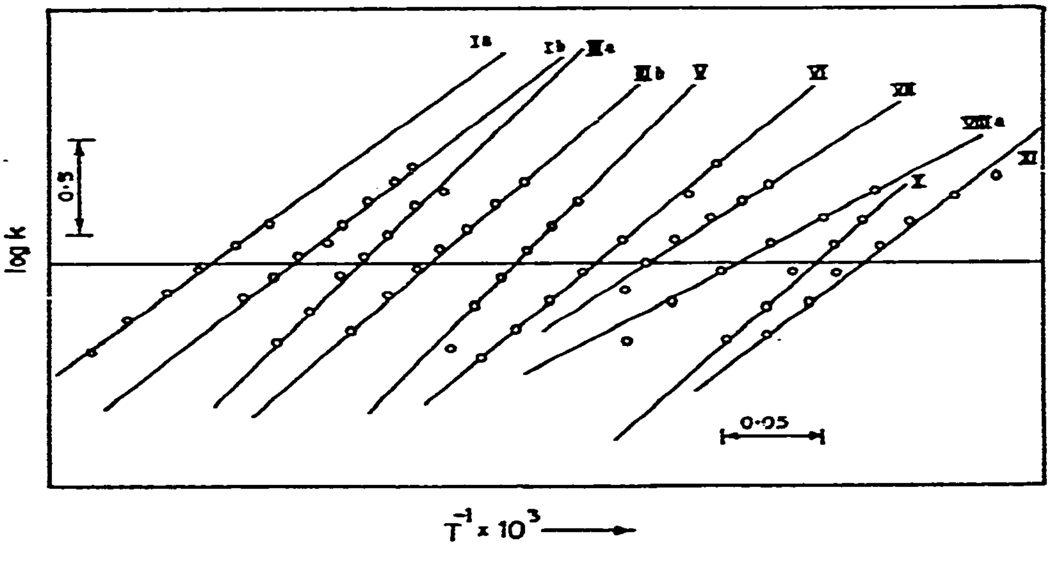

Fig. 7. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from the DTG curves for the decomposition of $MnCl_2 \cdot 0.50THP$ → $MnCl_2 \cdot 0.25THP$(Ia), $MnCl_2 \cdot 0.25THP$ → $MnCl_2$(Ib), $CoCl_2 \cdot 0.50THP$ → $CoCl_2 \cdot 0.25THP$(IIIa), $CoCl_2 \cdot 0.25THP$ → $CoCl_2$(IIIb), $NiCl_2 \cdot 0.20THP$ → $NiCl_2$(V), $NiBr_2 \cdot 0.10THP$ → $NiBr_2$(VI), $CuCl_2 \cdot 0.50THP$ → $CuCl_2$(VII), $CuBr_2 \cdot 1.00THP$ → $CuBr_2 \cdot 0.88THP$(VIIIa), $CdCl_2 \cdot 0.20THP$ → $CdCl_2$(X) and $CdBr_2 \cdot 1.00THP$ → $CdBr_2$(XI).

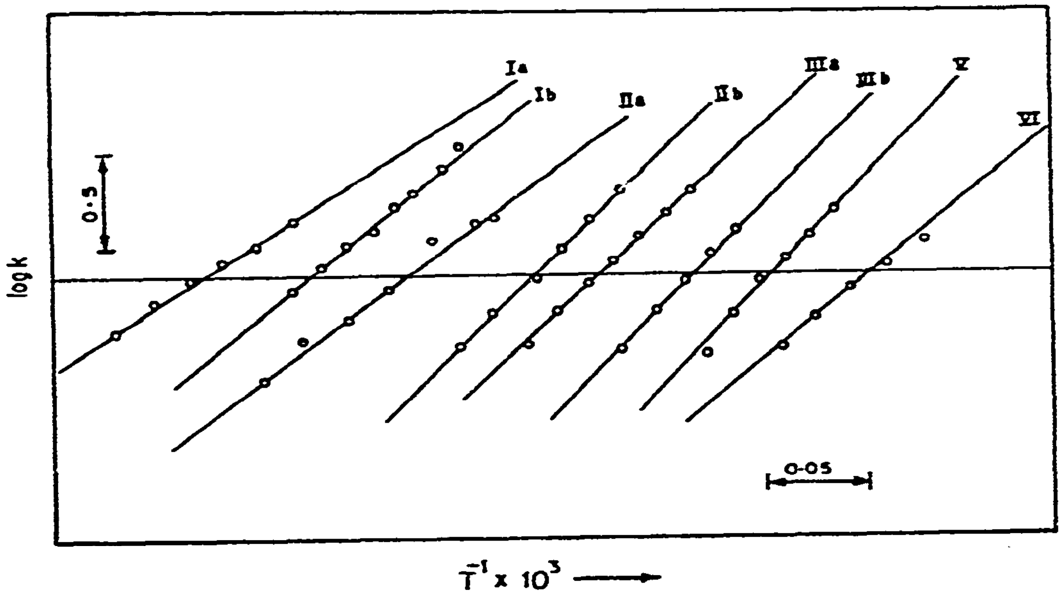

Fig. 8. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from the DTA curves for the decomposition of $MnCl_2 \cdot 0.50THP \rightarrow MnCl_2 \cdot 0.25THP$(Ia), $MnCl_2 \cdot 0.25THP \rightarrow MnCl_2$(Ib), $MnBr_2 \cdot 0.75THP \rightarrow MnBr_2 \cdot 0.60THP$(IIa), $MnBr_2 \cdot 0.60THP \rightarrow MnBr_2$(IIb), $CoCl_2 \cdot 0.50THP \rightarrow CoCl_2 \cdot 0.25THP$(IIIa), $CoCl_2 \cdot 0.25THP \rightarrow CoCl_2$(IIIb), $NiCl_2 \cdot 0.20THP \rightarrow NiCl_2$(V) and $NiBr_2 \cdot 0.10THP \rightarrow NiBr_2$(VI).

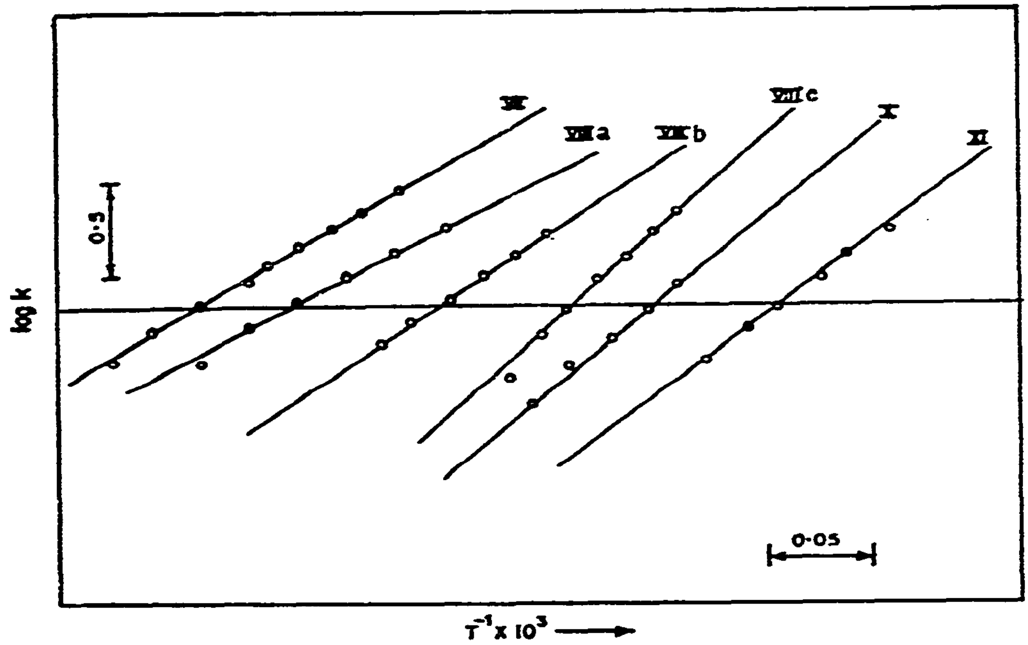

Fig. 9. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from the DTA curves for the decomposition of $CuCl_2 \cdot 0.50THP \rightarrow CuCl_2$(VII), $CuBr_2 \cdot 1.00THP \rightarrow CuBr_2 \cdot 0.88THP$(VIIIa), $CuBr_2 \cdot 0.88THP \rightarrow CuBr_2 \cdot 0.68THP$(VIIIb), $CuBr_2 \cdot 0.68THP \rightarrow CuBr_2$(VIIIc), $CdCl_2 \cdot 0.20THP \rightarrow CdCl_2$(X) and $CdBr_2 \cdot 1.00THP \rightarrow CdBr_2$(XI).

The decomposition reactions of all the adducts are endothermic. Temperature ranges of decomposition and the DTG peak temperatures for the adducts are listed in the second and third columns in Table 1, respectively. The enthalpy change for each step of decomposition of the adducts was evaluated by the method of Sano[13] using copper sulphate pentahydrate as the standard and the values are tabulated in the last column in Table 1. When the two DTA curves overlap too much with each other, the ΔH 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[14] equation. The values are tabulated in the fourth column of Table 1 and the plots of $\Delta \log (\mathrm{d}w/\mathrm{d}t)/\Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from TG curves are shown in Figs. 5 and 6.

The activation energy for each step of decomposition was also evaluated from the analysis of the DTG curve using the method of Dave and Chopra[15] and the method described in our earlier work[8] and also from the analysis of DTA curve using Borchardt's[16] equation for first order reaction and the values are tabulated in the fifth and sixth columns in Table 1, respectively, and the Arrhenius plots of $\log k$ vs. $T^{-1} \times 10^3$ from DTG and DTA curves are shown in Figs. 7–9.

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

DISCUSSION

Earlier, we isolated the adduct of $MnCl_2$ with oxo-compounds like tetrahydrofuran[9] and ethylene glycol dimethyl ether[10] whose composition corresponds to the adduct of this salt with tetrahydropyran. The nature of thermal decomposition of $MnCl_2 \cdot 0.50THP$, i.e., formation of an intermediate $MnCl_2 \cdot 0.25THP$ is also similar to that of tetrahydrofuran and ethylene glycol dimethyl ether. Whereas, the composition of the same salt with di-isopropyl ether[11] isolated by us differs from the present adduct, although the way of decomposition is similar. But the adduct with dioxan[8] differs not only in composition but also in nature of decomposition. The thermal stability of $MnCl_2 \cdot 0.50THP$ is close to that of tetrahydrofuran[9] and $MnCl_2 \cdot 0.40DIPE$ and is low with respect to the corresponding ethylene glycol dimethyl ether[10]. Whereas, the thermal stability of $MnCl_2 \cdot 0.25THP$ is high with respect to $MnCl_2 \cdot 0.25L$ where L is THF or EGDME and is close to $MnCl_2 \cdot 0.20DIPE$. We did not observe earlier the existence of any intermediate in the thermogram of the adduct of the same salt with dioxan like the adducts with oxo-compounds studied by us. The thermal stabilities of the adduct of this salt with the present oxo-compound and the other oxo-compounds studied earlier, irrespective of composition, reveal that the adduct with dioxan is thermally most stable. The activation energy* for the decomposition of $MnCl_2 \cdot 0.50THP \rightarrow MnCl_2 \cdot 0.25THP$ is low with respect to that of

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*Average of the values obtained from TG, DTG and DTA curves.

tetrahydrofuran and is high with respect to that of ethylene glycol dimethyl ether, whereas, the value of activation energy for the decomposition of $MnCl_2 \cdot 0.40DIPE \rightarrow MnCl_2 \cdot 0.20DIPE$ is high with respect to the adduct of this salt with the present oxo-compound and the adducts with oxo-compounds studied by us. Whereas, the activation energy for the decomposition of $MnCl_2 \cdot 0.25THP \rightarrow MnCl_2$ is lower than that of tetrahydrofuran and ethylene glycol dimethyl ether. For the decomposition of $MnCl_2 \cdot 0.20DIPE \rightarrow MnCl_2$ it is also high with respect to the value evaluated for the decomposition of the intermediate of $MnCl_2 \cdot 0.50THP$. The value of enthalpy change for the first step of decomposition of $MnCl_2 \cdot 0.50THP$ is high with respect to the adduct which has a similar composition as tetrahydrofuran and ethylene glycol dimethyl ether and is low with respect to the decomposition of $MnCl_2 \cdot 0.40DIPE$. Whereas, the value of enthalpy change for the decomposition of $MnCl_2 \cdot 0.25THP$ is also high with respect to that of tetrahydrofuran and ethylene glycol dimethyl ether and the value is low with respect to the value for the decomposition $MnCl_2 \cdot 0.20DIPE \rightarrow MnCl_2$. The value of enthalpy change of the adduct of the salt with dioxan was found to be low. This is probably due to the adduct having the oxo-compound in simple ratio.

The composition of the adduct $MnBr_2 \cdot 0.75THP$ differs from the adduct of this salt with dioxan, tetrahydrofuran, ethylene glycol dimethyl ether and di-isopropyl ether. It was observed earlier that other oxo-compounds studied by us produced adducts with a simple composition except di-isopropyl ether. The thermal stability with respect to the first DTG peak temperature of the adduct $MnBr_2 \cdot 0.75THP$ and the adduct of this salt with the other oxo-compounds studied by us follows an order irrespective of their composition EGDME>D>THP>DIPE>THF. Similarly the value of activation energy for the first step of decomposition of the tetrahydropyran adduct and the adducts with other oxo-compounds follows the order: THP> DIPE≈EGDME >THF>D. The enthalpy change for the decomposition of $MnBr_2 \cdot 0.75THP \rightarrow MnBr_2 \cdot 0.60THP$ is high in comparison to the values evaluated for the decomposition of adducts with dioxan, tetrahydrofuran and ethylene glycol dimethyl ether but is low with respect to the adduct with di-isopropyl ether. The comparative high value for tetrahydropyran and di-isopropyl ether in comparison to the adducts of this salt with oxo-compounds studied by us is probably due to the presence of the oxo-compound in fraction.

The composition of the adduct of $CoCl_2$ with tetrahydropyran is similar to that of dioxan, tetrahydrofuran and ethylene glycol dimethyl ether. The nature of thermal decomposition is also similar, though the adduct with dioxan showed decomposition in a single step observed from the respective thermogram but its corresponding DTA curve indicated the existence of an intermediate. Whereas, the adduct with di-isopropyl ether showed decomposition via an intermediate $CoCl_2 \cdot 0.20DIPE$ upon heating. The thermal stability of the adduct $CoCl_2 \cdot 0.50L$ where L = dioxan, tetrahydrofuran, ethylene glycol dimethyl ether and tetrahydropyran follows the order: D>THP = EGDME>THF. It is observed that the thermal stability of $CoCl_2 \cdot 0.34DIPE$ is close to that of $CoCl_2 \cdot 0.50THF$. The value of activation energy for the decomposition of $CoCl_2 \cdot 0.50THP \rightarrow CoCl_2 \cdot 0.25THP$ is maximum in comparison to the value for the corresponding decomposition of adducts with EGDME and THF. It is also high with respect to the value for the decompositions of $CoCl_2 \cdot 0.50D \rightarrow CoCl_2$ and $CoCl_2 \cdot 0.34DIPE \rightarrow CoCl_2 \cdot 0.20DIPE$. The enthalpy change for the first step of decomposition of $CoCl_2 \cdot 0.50THP$ is high with respect to that of tetrahydrofuran and ethylene glycol dimethyl ether and is appreciably high with respect to the decomposition of $CoCl_2 \cdot 0.50D \rightarrow CoCl_2$, though the composition of the adduct of this salt with oxo-compounds studied by us except DIPE is similar. It is noticed that the value of enthalpy change for the first step of decomposition of $CoCl_2 \cdot 0.34DIPE$ is high with respect to the value for the $CoCl_2 \cdot 0.50THP \rightarrow CoCl_2 \cdot 0.25THP$. Thermal stabilities of the adducts $CoCl_2 \cdot 0.25L$ where L = THP, EGDME and THF are close to each other. It is observed that the thermal stability of the intermediate $CoCl_2 \cdot 0.20DIPE$ of the adduct $CoCl_2 \cdot 0.34DIPE$ is also close to that of $CoCl_2 \cdot 0.25L$ where L = THP, EGDME and THF. The activation energy for the decomposition of an intermediate of this adduct is slightly higher with respect to the decomposition of the adduct with EGDME and THF. Whereas, the value for the decomposition of $CoCl_2 \cdot 0.20DIPE \rightarrow CoCl_2$ is high with respect to the decomposition of $CoCl_2 \cdot 0.25THP \rightarrow CoCl_2$. The enthalpy change for the decomposition of the intermediate adduct with THP is high with respect to that of THF, EGDME and DIPE whose values are very close to each other.

The composition of the adduct of $CoBr_2$ with tetrahydropyran is similar to that of the adduct with EGDME. This type of composition is observed as an intermediate in the thermogram of $CoBr_2 \cdot 2.00D$. Earlier, we observed the adduct of this salt with ethylene glycol dimethyl ether which eliminated oxo-compound upon heating in three steps. Similarly, the adduct $CoBr_2 \cdot 1.00THP$ shows decomposition in three steps for the elimination of the oxo-compound but the compositions of the intermediates observed in the thermogram are not similar to that of EGDME. The elimination of the oxo-compound in three steps was also observed in the adduct of this salt with dioxan where the compositions of the intermediates are simple in comparison to those of THP ana EGDME. The thermal stability of this adduct is close to that of ethylene glycol dimethyl ether and is low with respect to $CoBr_2 \cdot 1.00D$. The enthalpy change for the first step of decomposition of this adduct is close to that of dicxan but for the latter step of decomposition the value is appreciably high. The composition of the intermediate $CoBr_2 \cdot 0.25THP$ is common, whereas, the composition like $CoBr_2 \cdot 0.55THP$ is not observed in the earlier work studied by us. The activation energy for the first step of decomposition of this adduct is low, whereas, for the second and third step of decomposition, the values are appreciably high with respect to the decompositions of adducts with dioxan and ethylene glycol dimethyl ether.

The composition of the adduct $NiCl_2 \cdot 0.20THP$ is similar to that of di-isopropyl ether. Earlier, we isolated the adduct of this salt with dioxan and EGDME in simple composition. Whereas, an adduct with tetrahydrofuran was isolated as $NiCl_2 \cdot 0.25THF$. The thermal stabilities, the values of activation energies and enthalpy changes for decompositions of the adducts with THP and DIPE are close, whereas, these thermal parameters of the adduct $NiCl_2 \cdot 0.20THP$ are high with respect to the adducts with dioxan, tetrahydrofuran and ethylene glycol dimethyl ether. In our earlier work[11] the activation energy for the decomposition of $NiCl_2 \cdot 0.20DIPE \rightarrow NiCl_2$ evaluated from the TG curve was appreciably low in comparison to the value evaluated from DTA and DTG curves. A similar phenomenon is observed in the evaluation of the activation energy for the decomposition of $NiCl_2 \cdot 0.20THP \rightarrow NiCl_2$.

The adduct of $NiBr_2$ with tetrahydropyran isolated by us is very interesting. We never encountered this type of composition in our earlier works[8–11]. The composition of the adduct of this salt with THF and DIPE was also interesting. Whereas, the adducts with dioxan and ethylene glycol dimethyl ether were isolated in simple composition. The thermal stability of this adduct occupies the following position amongst the adducts irrespective of composition with oxo-compounds studied previously as $D > DIPE > THP \geqslant EGDME > THF$. The activation energy and enthalpy change of this adduct are high in comparison to those of the adducts of this salt with other oxo-compounds studied earlier, though the enthalpy change for the decomposition of $NiBr_2 \cdot 0.10THP \rightarrow NiBr_2$ is low with respect to that of the decomposition $NiBr_2 \cdot 0.44DIPE \rightarrow NiBr_2$.

Till now we could not isolate the adduct of $CuCl_2$ with oxo-compound in simple composition. The adduct of this salt with the present oxo-compound isolated by us is similar in composition to that of EGDME and also in the nature of decomposition. This type of composition is observed in the thermogram of $CuCl_2 \cdot 0.70THF$ as a thermally unstable intermediate. Whereas, dioxan produced an adduct $CuCl_2 \cdot 0.75D$ which lost the oxo-compound in a single step and di-isopropyl ether produced an adduct $CuCl_2 \cdot 0.25DIPE$ which also lost the oxo-compound in a single step. Only the adduct with tetrahydrofuran lost the oxo-compound in three steps passing through the following intermediates $CuCl_2 \cdot 0.50THF$ and $CuCl_2 \cdot 0.15THF$. The value of activation energy for the decomposition of $CuCl_2 \cdot 0.50THP$ does not differ much from the values evaluated for the decomposition of adducts with oxo-compounds studied by us. But the value of enthalpy change is appreciably high in comparison to the values for the decomposition of adducts of the same salt with the oxo-compounds studied by us. The thermal stability of this adduct is appreciably lower with respect to the adduct with dioxan and is high with respect to the adducts with THF, EGDME and DIPE.

We isolated the adduct of $CuBr_2$ with this oxo-compound in simple composition like the adduct with dioxan, tetrahydrofuran, ethylene glycol dimethyl ether and di-isopropyl ether. The composition of this adduct is similar to the adducts with oxo-compounds studied previously, though dioxan produced the adduct as $CuBr_2 \cdot 2.00D$ whose thermogram showed the existence of $CuBr_2 \cdot 1.00D$. Earlier, the elimination of oxo-compounds from the adducts which were similar in composition to this adduct took place in a single step observed from the respective thermogram. Whereas, the present adduct loses the oxo-compound in three steps. The compositions of the intermediates observed from the thermogram of $CuBr_2 \cdot 1.00THP$ are very interesting.

The thermal stability of this adduct is very low in comparison to the other adducts of the same salt with the oxo-compounds studied by us and the order of the thermal stabilities of the adducts $CuBr_2 \cdot 1.00L$ where L represents the oxo-compounds already studied by us is as follows: DIPE>THF>EGDME>D>THP. The value of activation energy for the first step of decomposition of $CuBr_2 \cdot 1.00THP$ does not differ much from the values for the decomposition of adducts with oxo-compounds reported earlier. But the value of enthalpy change is appreciably higher in comparison to those of adducts with dioxan, tetrahydrofuran etc. This noticeable difference in the value of enthalpy change of this adduct from the other adducts of this salt is probably due to the elimination of the oxo-compound in complex fashion.

We isolated the adduct of $CdCl_2$ with this oxo-compound in two compositions. The adduct $CdCl_2 \cdot 0.20THP$ is isolated by keeping the adduct $CdCl_2 \cdot 0.75THP$ in a vacuum desiccator for long hours. Earlier[8], by adopting this technique we isolated the two adducts of $NiBr_2$ with dioxan, i.e., $NiBr_2 \cdot 2.00D$ and $NiBr_2 \cdot 1.00D$. However, the compositions of both the adducts with THP isolated by us are not similar to the adducts with other oxo-compounds studied earlier. Earlier, it was observed that the elimination of oxo-compounds from the adducts of this salt took place in a single step. Similarly here also both the adducts lose the oxo-compound in a single step. We expected the existence of the adduct $CdCl_2 \cdot 0.20THP$ in the thermogram of $CdCl_2 \cdot 0.75THP$ but in actual practice we could not find it. Similarly, in the thermogram of $NiBr_2 \cdot 2.00D$, the existence of $NiBr_2 \cdot 1.00D$ was not indicated in the thermogram of $NiBr_2 \cdot 2.00D$. The thermal stabilities of $CdCl_2 \cdot 0.75THP$ and the adducts of this salt with other oxo-compounds follow the order: D>THP$\geqslant$THF>EGDME. It is also observed that the thermal stabilities of the adducts $CdCl_2 \cdot 0.75THP$ and $CdCl_2 \cdot 0.20THP$ differ slightly. Whereas, the activation energies and enthalpy changes differ appreciably. The value of activation energy for the decomposition of $CdCl_2 \cdot 0.75THP \rightarrow CdCl_2$ is close to that of the adduct with EGDME. The value is slightly lower with respect to the adduct with THF and is appreciably lower with respect to the adduct with dioxan. The values of enthalpy changes for the decomposition of $CdCl_2 \cdot 0.75THP \rightarrow CdCl_2$ and the adducts with tetrahydrofuran and dioxan are close to each other. But the value of enthalpy change for the adduct with EGDME is high with respect to that of the adduct with THP.

Till now we isolated the adduct of $CdBr_2$ in simple composition, i.e., $CdBr_2 \cdot 1$ (oxo-compound). Like the decomposition of adducts with other oxo-compounds, here also elimination of oxo-compound takes place in a single step. The thermal stability of this adduct is close to that of THF and EGDME but is appreciably lower with respect to that of dioxan. The value of enthalpy change for the decomposition of this adduct is close to those of dioxan, tetrahydrofuran and ethylene glycol dimethyl ether. But the value of activation energy is slightly higher in comparison to the values of adducts with dioxan, ethylene glycol dimethyl ether and tetrahydrofuran.

The thermal stability of the adducts of metal chloride, irrespective of composition with respect to the first DTG peak temperature, increases in the order: Ni>Co>Mn>Cd>Cu. It is observed that the thermal stability of the adduct

$NiCl_2 \cdot 0.20THP$ is appreciably higher in comparison to the other metal chloride adducts. On the other hand the thermal stabilities of the adducts of metal bromide irrespective of composition are very close to each other except the adduct $CuBr_2 \cdot 1.00THP$.

It is observed in our earlier works that for the adduct molecules of metallic halides with oxo-compounds, which lose the oxo-compound in more than one step, the activation energy for the latter step of decomposition gives a larger value than the earlier. The adduct molecules of this oxo-compound show a similar phenomenon, except in the decomposition of $CoCl_2 \cdot 0.50THP$ where activation energies of the former step of decomposition $CoCl_2 \cdot 0.50THP \rightarrow CoCl_2 \cdot 0.25THP$ and the latter step of decomposition $CoCl_2 \cdot 0.25THP \rightarrow CoCl_2$ are close to each other. The variation in the values of activation energy for the decomposition of adducts evaluated from TG, DTG and DTA curves is not too much, though an appreciable low activation energy value is observed from the analysis of TG curves of $NiCl_2 \cdot 0.20THP \rightarrow NiCl_2$ and $CdBr_2 \cdot 1.00THP \rightarrow CdBr_2$ in comparison to the values obtained from the respective DTA or DTG curves.

In the present paper the values of enthalpy changes of decomposition of the adduct molecules range from ~8–~85 kcal mol^{-1}. It is noticed that the value of enthalpy change is low, i.e., 19.5 kcal mol^{-1} where, the composition of the adduct is simple i.e., $CdBr_2 \cdot 1.00THP$ and the value is high, i.e., 84.2 kcal mol^{-1} where, the composition of the adduct is not simple, i.e., $NiBr_2 \cdot 0.10THP$. The same phenomenon is also observed in the decomposition of adduct molecules with di-isopropyl ether studied earlier. But in the decomposition of $CuBr_2 \cdot 1.00THP \rightarrow CuBr_2 \cdot 0.88THP$ the enthalpy change is high, i.e., 73.0 kcal mol^{-1}, though the composition of the adduct is simple. The probable explanation is already stated in the text. In general the latter step of decomposition gives a larger ΔH value than the earlier step. But such tendencies are not observed in the decomposition of all the adducts. On the contrary, an appreciable decrease in the value of enthalpy change is observed for the latter step of decomposition in comparison to the earlier step in the case of the adduct $CuBr_2 \cdot 1.00THP$.

Till now we carried out the thermal decomposition of adducts of metallic halides with oxo-ethers. Though these ethers show differences in molecular volumes, nature of chain (open or closed), number of adduct formation centre, etc., some similarities are observed with respect to the composition and thermal properties amongst the adduct molecules of oxo-compounds studied by us.

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