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

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ABSTRACT

Non-isothermal studies of some adduct molecules of metallic halides with di-isopropyl ether as the type $MX_2(DIPE)_y$ in solid state, were carried out with a derivatograph, where M = Mn(II), Co(II), Ni(II) or Cu(II), $X = Cl^-$ or Br^-. DIPE = di-isopropyl ether and $y = 0.2-1$. These adduct molecules lost di-isopropyl 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 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 and ethylene glycol dimethyl ether.

INTRODUCTION

The work on the adduct molecules with di-isopropyl ether has been carried out by a few workers[1,2]. They only prepared and characterised some adduct molecules of metallic halides with this oxo-compound. But none of them investigated the thermal properties of the adducts by thermogravimetry, differential thermal analysis and differential thermogravimetric analysis and they did not evaluate the activation energy, the order of reaction and the enthalpy change for each step of decomposition. We reported earlier non-isothermal studies of adduct molecules of metallic halides with oxo-compounds like dioxan[3], tetrahydrofuran[4] and ethylene glycol dimethyl ether[5]. In continuation to these works this paper deals with the thermal decomposition of di-isopropyl ether adducts of some metal halides to evaluate the activation energy of decomposition by the 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[3–5].

EXPERIMENTAL

For the preparation of the di-isopropylether adducts of metal halides, anhydrous di-isopropyl ether was added in excess to the finely powdered anhydrous metal halides and the mixture was refluxed for 24–48 h under dry conditions. The mixture was then kept in a desiccator for slow evaporation of excess di-isopropyl ether. All the adducts were characterised by elemental analysis and IR spectral measurement. The di-isopropyl ether used was sufficiently purified and dried according to the standard procedure[6].

The following adducts of metal halides were prepared: (1) $MnCl_2 \cdot 0.40DIPE$; (2) $MnBr_2 \cdot 0.36DIPE$; (3) $CoCl_2 \cdot 0.34DIPE$; (4) $NiCl_2 \cdot 0.20DIPE$; (5) $NiBr_2 \cdot 0.36DIPE$; (6) $CuCl_2 \cdot 0.25DIPE$; (7) $CuBr_2 \cdot 1.00DIPE$, where DIPE denotes di-isopropyl ether.

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 samples 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

Figure 1 shows the derivatograms of $MnCl_2 \cdot 0.4DIPE$ and $MnBr_2 \cdot 0.36DIPE$. The adduct $MnCl_2 \cdot 0.40DIPE$ loses the oxo-compound in two steps passing through a thermally stable intermediate $MnCl_2 \cdot 0.20DIPE$, whereas, the adduct $MnBr_2 \cdot 0.36DIPE$ loses the oxo-compound in three steps, i.e., $MnBr_2 \cdot 0.36DIPE \rightarrow MnBr_2 \cdot 0.23DIPE \rightarrow MnBr_2 \cdot 0.16DIPE \rightarrow MnBr_2$. None of the intermediates are thermally stable. Though the composition of the adduct $CoCl_2 \cdot 0.34DIPE$ differs from $MnCl_2 \cdot 0.40DIPE$, it gives an intermediate, i.e., $CoCl_2 \cdot 0.20DIPE$ which is similar in composition to the corresponding intermediate of the adduct of $MnCl_2$. The adducts of $NiCl_2$ and $NiBr_2$ with di-isopropyl ether lose the oxo-compound in a single step upon heating observed from the respective derivatogram (Fig. 2) whereas, the adducts $CuCl_2 \cdot 0.25DIPE$ and $CuBr_2 \cdot 1.00DIPE$ show a single step decomposition indicated from their TG curves (Fig. 3). But their corresponding DTA and DTG curves indicate the existence of a thermally unstable intermediate product.

The decomposition of all the adducts shows an endothermic reaction. Temperature ranges of decomposition and the DTG peak temperatures for the adducts are listed in the second and third columns of Table 1, respectively. The enthalpy change for each step of decomposition of the adducts was evaluated by the method of Sano[7] using copper sulfate 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[8]

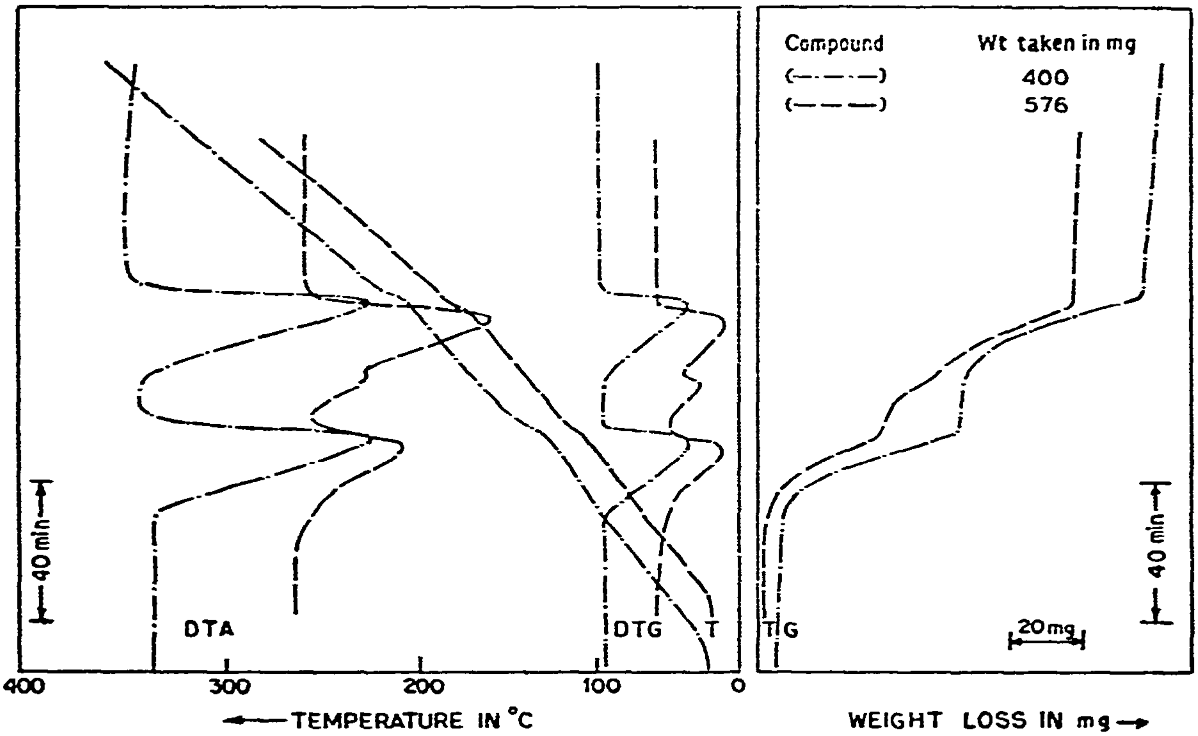

Fig. 1. Derivatograms for the decomposition of $MnCl_2 \cdot 0.4DIPE$ (—·—·—) and $MnBr_2 \cdot 0.36DIPE$ (— — —).

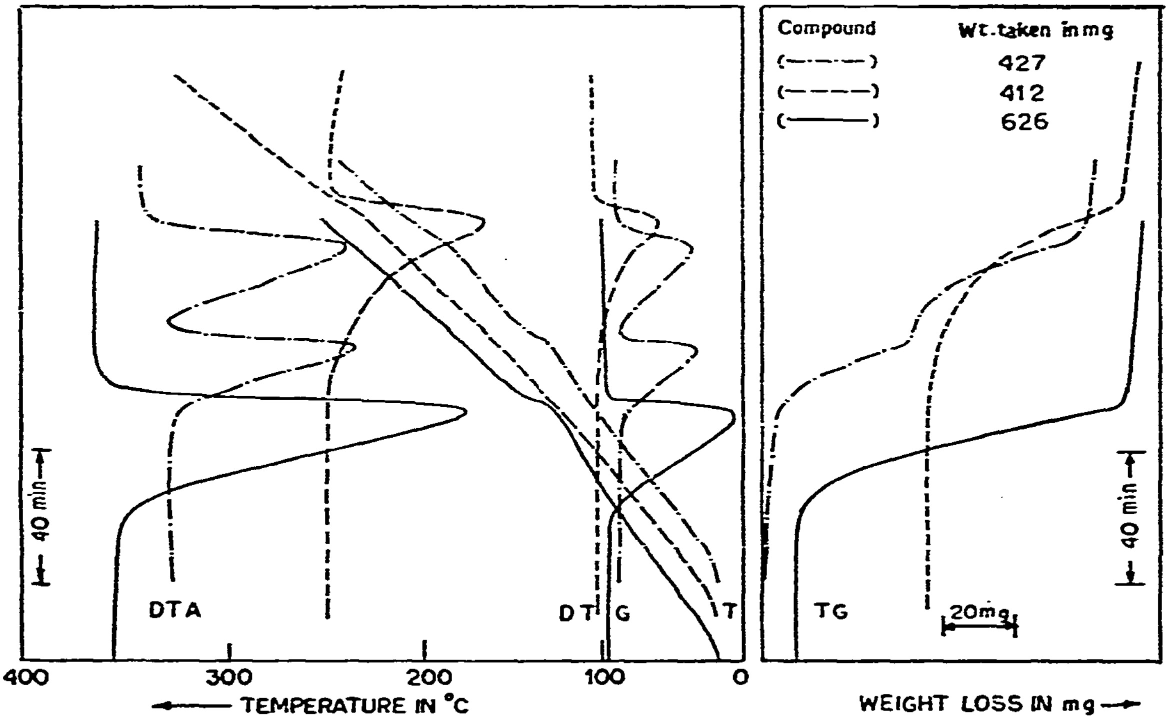

Fig. 2. Derivatograms for the decomposition of $CoCl_2 \cdot 0.34DIPE$ (—·—·—), $NiCl_2 \cdot 0.2DIPE$ (— — —) and $NiBr_2 \cdot 0.36DIPE$ (———).

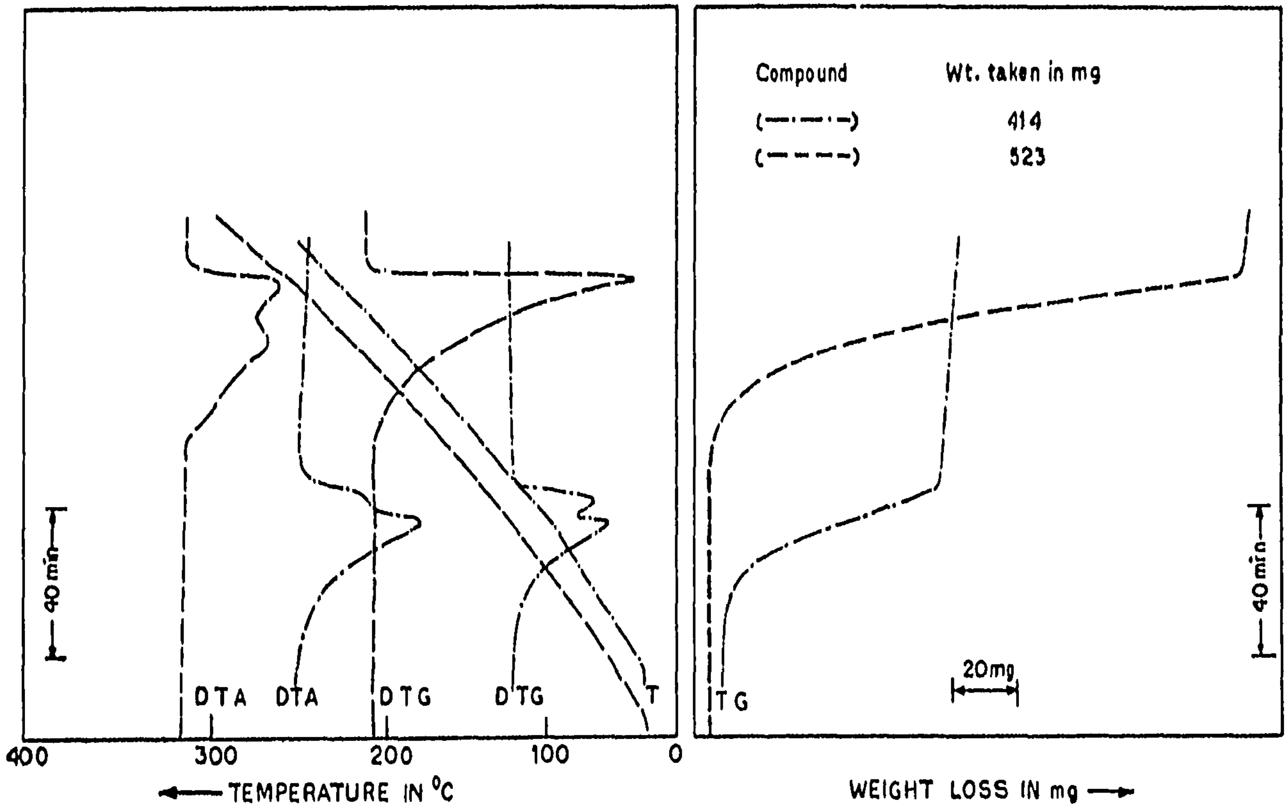

Fig. 3. Derivatograms for the decomposition of $CuCl_2 \cdot 0.25DIPE$ (—·—·—) and $CuBr_2 \cdot 1DIPE$ (— — —).

TABLE 1

THERMAL PARAMETERS FOR THE DECOMPOSITION OF ADDUCT MOLECULES OF SOME METALLIC HALIDES WITH DI-ISOPROPYL ETHER

L denotes di-isopropyl ether.

Decomposition reactions		*Temp. range (°C)*	*DTG peak temp. (°C)*	*Activation energy (kcal mol^{-1})*			*Enthalpy change (kcal mol^{-1})*
				TG	*DTG*	*DTA*	
(Ia)	$MnCl_2 \cdot 0.40L \rightarrow MnCl_2 \cdot 0.20L$	98–135	127	46.0	46.0	46.0	81.7
(Ib)	$MnCl_2 \cdot 0.20L \rightarrow MnCl_2$	163–214	205	46.0	46.0	46.0	81.7
(IIa)	$MnBr_2 \cdot 0.36L \rightarrow MnBr_2 \cdot 0.23L$	60–108	101	36.8	36.8	30.0	56.2
(IIb)	$MnBr_2 \cdot 0.23L \rightarrow MnBr_2 \cdot 0.16L$	108–145	137	73.6	—	—	67.1[a]
(IIc)	$MnBr_2 \cdot 0.16L \rightarrow MnBr_2$	145–178	168	128.8	—	—	
(IIIa)	$CoCl_2 \cdot 0.34L \rightarrow CoCl_2 \cdot 0.20L$	93–135	127	46.0	46.0	46.0	70.2
(IIIb)	$CoCl_2 \cdot 0.20L \rightarrow CoCl_2$	142–204	185	57.5	57.5	57.5	56.9
(IV)	$NiCl_2 \cdot 0.20L \rightarrow NiCl_2$	180–255	228	28.3	53.6	53.6	71.7
(V)	$NiBr_2 \cdot 0.36L \rightarrow NiBr_2$	79–140	125	36.8	36.8	36.8	94.2
(VI)	$CuCl_2 \cdot 0.25L \rightarrow CuCl_2$	50–120	95	18.4	—	—	45.1[a]
(VII)	$CuBr_2 \cdot 1.00L \rightarrow CuBr_2$	167–265	253	30.6	30.6	—	19.6[a]

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

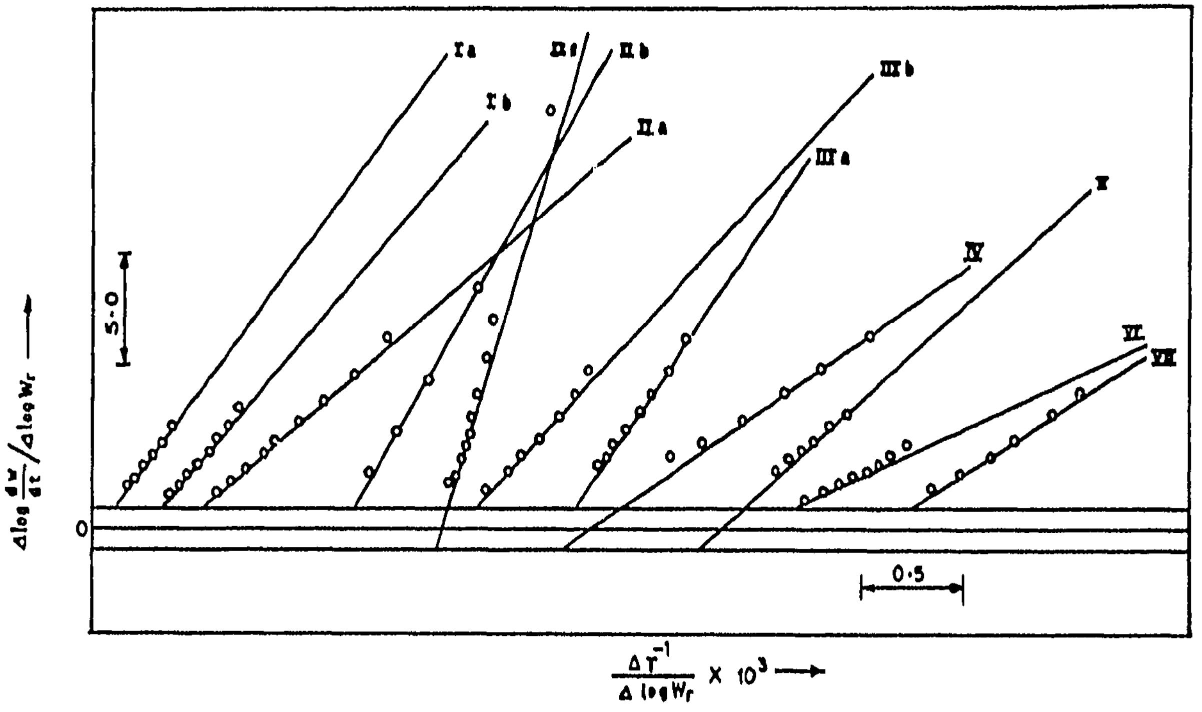

Fig. 4. Plots of $\Delta \log \frac{dw}{dt} \Big/ \Delta \log W_r$ vs. $\Delta T^{-1}/\Delta \log W_r \times 10^3$ from the TG curves for the decomposition of $MnCl_2 \cdot 0.4DIPE \rightarrow MnCl_2 \cdot 0.2DIPE$ (Ia), $MnCl_2 \cdot 0.2DIPE \rightarrow MnCl_2$ (Ib), $MnBr_2 \cdot 0.36DIPE \rightarrow MnBr_2 \cdot 0.23DIPE$ (IIa), $MnBr_2 \cdot 0.23DIPE \rightarrow MnBr_2 \cdot 0.16DIPE$ (IIb), $MnBr_2 \cdot 0.16DIPE \rightarrow MnBr_2$ (IIc), $CoCl_2 \cdot 0.34DIPE \rightarrow CoCl_2 \cdot 0.2DIPE$ (IIIa), $CoCl_2 \cdot 0.2DIPE \rightarrow CoCl_2$ (IIIb), $NiCl_2 \cdot 0.2DIPE \rightarrow NiCl_2$ (IV), $NiBr_2 \cdot 0.36DIPE \rightarrow NiBr_2$ (V), $CuCl_2 \cdot 0.25DIPE \rightarrow CuCl_2$ (VI) and $CuBr_2 \cdot 1DIPE \rightarrow CuBr_2$ (VII).

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 Fig. 4.

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[9] and the method described in our earlier work[3] and also from the analysis of the DTA curve using Brochardt's[10] equation for first order reaction and the values are tabulated in the fifth and sixth columns of 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. 5 and 6, respectively.

IR spectra of the adducts were taken to ensure the presence of the di-isopropyl ether molecule in the adduct.

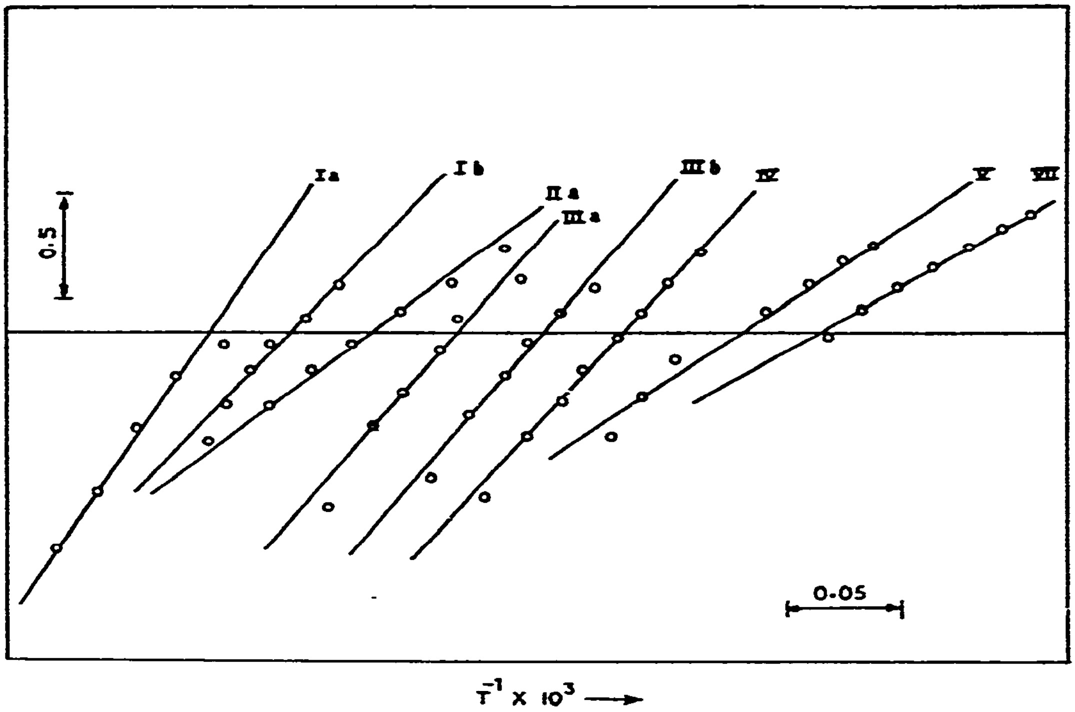

Fig. 5. Arrhenius plots of $\log k$ vs. $T^{-1} \times 10^3$ from the DTG curves for the decomposition of $MnCl_2 \cdot 0.4DIPE \rightarrow MnCl_2 \cdot 0.2DIPE$(Ia), $MnCl_2 \cdot 0.2DIPE \rightarrow MnCl_2$(Ib), $MnBr_2 \cdot 0.36DIPE \rightarrow MnBr_2 \cdot 0.23DIPE$(IIa), $CoCl_2 \cdot 0.34DIPE \rightarrow CoCl_2 \cdot 0.2DIPE$(IIIa), $CoCl_2 \cdot 0.2DIPE \rightarrow CoCl_2$(IIIb), $NiCl_2 \cdot 0.2DIPE \rightarrow NiCl_2$(IV), $NiBr_2 \cdot 0.36DIPE \rightarrow NiBr_2$(V) and $CuBr_2 \cdot 1DIPE \rightarrow CuBr_2$(VII).

DISCUSSION

Earlier, we studied the adduct of $MnCl_2$ with dioxan[3], tetrahydrofuran[4] and ethylene glycol dimethyl ether[5]. None of these oxo-compounds produced an adduct of the composition like $MnCl_2 \cdot 0.40DIPE$. The adduct $MnCl_2 \cdot 0.40DIPE$ produces an intermediate product, i.e., $MnCl_2 \cdot 0.20DIPE$ upon heating like the

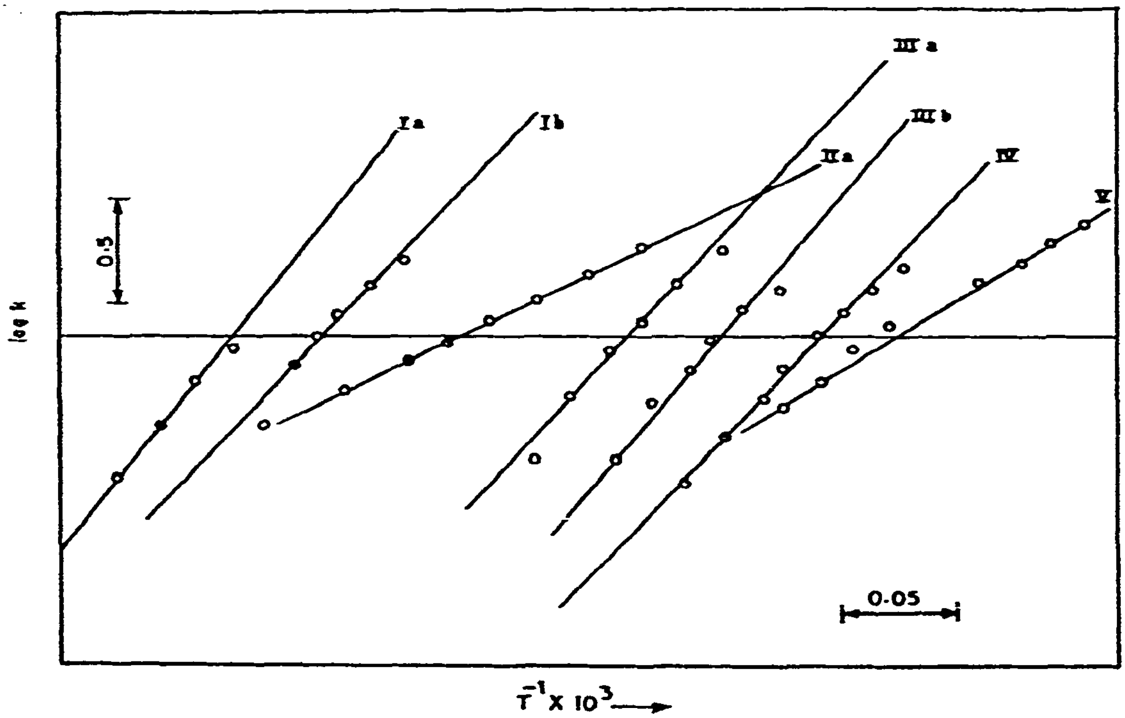

Fig. 6. Arrhenius plots of log k vs. $T^{-1} \times 10^3$ from the DTA curves for the decomposition of $MnCl_2 \cdot 0.4DIPE \rightarrow MnCl_2 \cdot 0.2DIPE$(Ia), $MnCl_2 \cdot 0.2DIPE \rightarrow MnCl_2$(Ib), $MnBr_2 \cdot 0.36DIPE \rightarrow MnBr_2 \cdot 0.23DIPE$(IIa), $CoCl_2 \cdot 0.34DIPE \rightarrow CoCl_2 \cdot 0.2DIPE$(IIIa), $CoCl_2 \cdot 0.2DIPE \rightarrow CoCl_2$(IIIb), $NiCl_2 \cdot 0.2DIPE \rightarrow NiCl_2$(IV) and $NiBr_2 \cdot 0.36DIPE \rightarrow NiBr_2$(V).

corresponding adduct of tetrahydrofuran and ethyleneglycol dimethyl ether, though the composition of the intermediate differs from that of tetrahydrofuran and ethylene glycol dimethyl ether. The thermal stability of this adduct is close to that of tetrahydrofuran and lower than that of dioxan and ethylene glycol dimethyl ether. The activation energy and enthalpy change of decomposition are high with respect to the corresponding adduct of oxo-compounds studied by us[3-5]. The thermal stability of $MnCl_2 \cdot 0.20DIPE$ is high in comparison with the intermediate adduct of THF and EGDME. Here also the value of enthalpy change of decomposition is high in comparison to that of tetrahydrofuran and ethylene glycol dimethyl ether but the value of activation energy is low. We attempted to isolate this adduct which is similar in composition to tetrahydrofuran observing a similar pattern of decomposition but could not succeed. The composition and thermal properties of this adduct disclose a view that with respect to $MnCl_2$ the adduct forming ability of ethylene glycol dimethyl ether and tetrahydrofuran is close but is low for di-isopropyl ether, though the thermal stability of the intermediate product $MnCl_2 \cdot 0.20DIPE$ tells the reverse.

The composition of the adduct $MnBr_2 \cdot 0.36DIPE$ is different from the corresponding adducts with oxo-compounds studied earlier[3-5]. Its nature of decomposition is also different. We attempted repeatedly to isolate the adduct of this salt in simple composition like the corresponding adduct with dioxan, tetrahydrofuran and ethylene glycol dimethyl ether. The thermal stability of this adduct is low with respect to the corresponding adduct with dioxan and ethylene glycol dimethyl ether and is high with respect to that of tetrahydrofuran. The activation energy and enthalpy change of decomposition are high in comparison to those of other oxo-compounds. The composition of this adduct and its intermediates is curious. So far we studied the inorganic adduct molecule, we did not observe the existence of adducts of such compositions.

Earlier, we isolated the adducts of $CoCl_2$ with dioxan, tetrahydrofuran and ethylene glycol dimethyl ether whose compositions were similar, i.e., $CoCl_2 \cdot 0.5L$, where L denotes the mentioned oxo-compounds. But with the present oxo-compound we could not isolate the adduct of this salt with a similar composition. It is noticed in our earlier work that the adduct of this salt with tetrahydrofuran and ethylene glycol dimethyl ether lost the oxo-compound in two steps passing through an intermediate $CoCl_2 \cdot 0.25L$, where L denotes tetrahydrofuran or ethylene glycol dimethyl ether. Though the composition of the adduct of this salt with di-isopropyl ether does not tally with the composition of the adduct of the same salt with tetrahydrofuran and ethylene glycol dimethyl ether, it decomposes similarly upon heating via an intermediate $CoCl_2 \cdot 0.20DIPE$. It may be mentioned that the type of composition of this intermediate adduct is not common to the adducts isolated by us earlier[3–5] but with the present oxo-compound we observed the existence of several adducts having the composition $MCl_2 \cdot 0.20DIPE$ where M = Mn(II), Co(II) or Ni(II).

The thermal stability of the adduct of $NiCl_2$ is much higher in comparison to the adducts with other oxo-compounds like tetrahydrofuran, ethylene glycol dimethyl ether and dioxan with the same salt. Similarly, its activation energy and enthalpy change of decomposition are also high. Till now we observe that the value of activation energy evaluated from the TG curve using Freeman and Carroll's equation is close to that of the value evaluated from DTA and DTG curves using Brochardt's equation for first order reaction and Dave and Chopra's method, respectively. But it is observed that the value of activation energy evaluated from the TG curve of $NiCl_2 \cdot 0.20DIPE$ using Freeman and Carroll's equation is noticeably low in comparison to the value evaluated from the corresponding DTA and DTG curves.

We isolated the adduct of $NiBr_2$ with dioxan and ethylene glycol dimethyl ether in simple composition. Whereas, the composition of the adduct of this salt with tetrahydrofuran is not simple like the corresponding adduct with the present oxo-compound. The single step of decomposition is observed in $NiBr_2 \cdot 0.44DIPE$ and also in the case of decompositions of adducts with other oxo-compounds of this salt. This adduct molecule is thermally more stable than the corresponding adduct with tetrahydrofuran and ethylene glycol dimethyl ether and less than the adduct with dioxan. Whereas, the value of activation energy and enthalpy change of decomposition is high in comparison to adducts of those oxo-compounds studied earlier[3–5].

We could not isolate the adduct of $CuCl_2$ with an oxo-compound like THF, dioxan, EGDME and DIPE in simple composition. The composition of the adduct of this salt with di-isopropyl ether is not common to the adducts with this oxo-compound, though this type of composition is found in many of the adducts isolated by us earlier. The thermal stability of this adduct is close to that of tetrahydrofuran and ethylene glycol dimethyl ether and is much lower with respect to the adduct of dioxan. Whereas, the activation energy and enthalpy change of decomposition of this adduct is high with respect to the adducts of this salt with other oxo-compounds studied earlier[3–5].

In case of $CuBr_2$, we isolated the adduct with di-isopropyl ether in simple composition, i.e., $CuBr_2 \cdot 1DIPE$ which is similar in composition to the corresponding adducts of other oxo-compounds studied by us. All the adducts lose oxo-compounds in a single step. The thermal stability of $CuBr_2 \cdot 1DIPE$ is close to that of tetrahydrofuran and ethylene glycol dimethyl ether but is very high with respect to that of dioxan. Its activation energy is low with respect to the corresponding adducts studied by us. But the enthalpy change is higher than that of dioxan and tetrahydrofuran and lower than that of ethylene glycol dimethyl ether.

We attempted repeatedly to isolate the adduct of $CdCl_2$ and $CdBr_2$ with this oxo-compound but could not succeed.

The DTG peak temperature for metal chloride adducts increases in the order $Cu > Mn = Co > Ni$ and for the adducts of metal bromide increases in the order $Mn > Ni > Cu$. These orders are irrespective of compositions. Whereas, the DTG peak temperature of the similar compositions, i.e., $MCl_2 \cdot 0.2DIPE$ where $M = Co$, Mn or Ni increases in the order $Co > Mn > Ni$.

The variation of the values of activation energy for the decomposition evaluated from TG, DTG and DTA curves is not too much except the decomposition of $NiCl_2 \cdot 0.2DIPE \rightarrow NiCl_2$. This shows that all the methods used for the evaluation of activation energy are standard. It is observed in our earlier works that for salt hydrates[11–13] and also for the inorganic adduct molecules with different oxo-compounds[3–6] which lose H_2O/oxo-compound in more than one step, the activation energy for the latter step of dehydration/decomposition gives a larger value than the earlier. The inorganic adduct molecules of this oxo-compound show a similar phenomenon, except in the decomposition of $MnCl_2 \cdot 0.2DIPE \rightarrow MnCl_2$, where the value of activation energy of the former step of decomposition $MnCl_2 \cdot 0.4DIPE \rightarrow MnCl_2 \cdot 0.2DIPE$ and of the latter step of decomposition are equal.

It is also observed that the value of enthalpy change of decomposition of the adduct molecules ranges from ~20–~95 kcal. It is noticed that the value of enthalpy change is considerably low, i.e., 19.6 kcal mol^{-1} where the composition of the adduct is simple, i.e., $CuBr_2 \cdot 1DIPE$ and the value is high, i.e., 94.2 kcal mol^{-1} where the composition of adduct is complicated, i.e., $NiBr_2 \cdot 0.36DIPE$. In our earlier work with the other oxo-compounds the maximum value of ΔH was not so high. This is probably due to the adducts isolated in more simple composition with respect to the present adduct molecules.

We found in our earlier work some similarities in composition and also in thermal properties amongst some of the adduct molecules of tetrahydrofuran and ethylene glycol dimethyl ether though these two oxo-compounds differ in molecular volume, number of adduct formation centre, etc. But with the present oxo-compound we did find a little similarity amongst the adduct molecules of other oxo-compounds studied earlier.

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