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THERMAL DECOMPOSITION OF COMPLEXES OF CADMIUM(II) AND MERCURY(II) WITH TRIPHENYLPHOSPHANES

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A series of substituted triphenylphosphane complexes of the type CdL_2X_2 (L= triorthotolylphosphane or trimetatolylphosphane; X=Cl^-, Br^- or I^-) and HgL_2X_2 (L=triphenylphosphane or triorthotolylphosphane) was prepared fresh. The thermal decomposition was carried out in air with heating rate programmed at 10°C min^{-1} and it revealed that the complexes with ortho derivative were less stable and the triphenylphosphane moiety leaves along with halogen in the first step. All the complexes were stable up to 210°C. However, the stability order of the tetrahedral complexes was X=Cl>Br. Values of n, E, ln$A$ and $\Delta S^{\#}$ have been approximated and compared. Complexes having Br have higher E_a, ln$A$ and $\Delta S^{\#}$ values than that having Cl.

Keywords: *activation energy, cadmium(II), complexes, entropy of activation, mercury(II), non-isothermal solid state decomposition, trimetatolylphosphane, triorthotolylphosphane, triphenylphosphane*

Introduction

Many authors investigated coordination compounds due to their chemical, biological, environmental, ion-exchange and catalytic importance and their thermal, spectral, microscopic and many other properties have also been examined [1–39]. The catalytic applications of a large number of phosphane based coordination compounds in processes such as hydrogenation, hydroformylation, hydrosilylation, hydrocyanation and oligomerization [40–44] have established the tertiary phosphanes particularly the triaryl ones among the choice ligands. Triphenylphosphanes have two great advantages over their trialkyl analogues. While the trialkylphosphanes are nasty smelling liquids, triphenylphosphane is an odourless solid with substantial stability and so is the case with other triarylphosphanes. Secondly, the greater σ-electron donor ability (basicity) of the trialkylphosphanes brings stability to the metal complexes. The greater steric bulk of the arylphosphanes and weaker bonding affinities with metals create an electronic environment that is conducive to formation of an empty or potentially reactive coordination site on the metal. The (2-methylphenyl)diphenylphosphane ligand, as part of a platinum catalyst has been found to be enhancing selectivity to the branched aldehyde in the hydroformylation of 2-butene [45]. Although the crowding affected the activity of the catalyst, the substituted phosphanes have gained much significance in recent times because of the steering effect of ortho substitution of aryl phosphane. The triaryl phosphane complexes of platinum group metals have been synthesized and somewhat studied but complexes of cadmium and mercury with substituted triarylphosphanes appear to have escaped attention of the workers so far. Secondly, the catalysts may have to be used at different temperatures and this created interest in taking up the thermal decomposition of a series of complexes of cadmium(II) and mercury(II) {CdX_2L_2 (L=triorthotolylphosphane (TOTP) i.e., tri(2-methylphenyl)phosphane or trimetatolylphosphane, TMTP i.e., tri(3-methylphenyl)phosphane: X= Cl^-, Br^- or I^-) and HgX_2L_2 (L=triphenylphosphane or triorthotolylphosphane)(tolyl=methylphenyl)}. Variation in the kinetic parameters that is observed [46, 47] with change in the metal and the ligand, has been tested. The thermogravimetric data have been subjected to mechanistic analysis and 15 kinetic models have been tested.

Experimental

Materials and methods

A series of complexes of cadmium(II) and mercury(II) {CdL_2X_2 (L=triorthotolylphosphane, TOTP or trimetatolylphosphane,TMTP; X=Cl^-, Br^- or I^-) and HgL_2X_2 (L=triphenylphosphane or triorthotolylphosphane)(tolyl=methylphenyl)}was prepared by mixing hot solutions of the anhydrous halides (X=Cl, Br, I) in absolute alcohol and that of the corresponding phosphane derivatives in appropriate molar ratios, followed by vigorous shaking on an electric shaker for about an hour in each case.The formations of the $CdL_2\ I_2$ precipitate and the $HgL_2\ X_2$ (L=TOTP) pre-

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cipitate, however, were rapid. The crystals of the complex formed were washed with ether and dried over air suction and recrystallized. The triphenylphosphane was of Eastman Kodak make. Cadmium chloride crystals ($CdCl_2$, $2.5H_2O$) were from Reanal and other chemicals were of Merck/BDH make. Anhydrous cadmium chloride and cadmium bromide were obtained by heating crystals of cadmium chloride and cadmium bromide ($CdBr_2$, $4H_2O$) in an air oven at 150°C for a few hours. The stoichiometries of the complexes were established on the basis of routine elemental analysis and molecular mass determination. Two series of diamagnetic complexes were isolated viz.: $(R_3P)_2$ $(MX)_2$ and $(R_3P)_2{\cdot}MX_2$ {*M*=Cd, Hg; *X*=Cl, Br, I; *R*=phenyl, 2-methylphenyl-(orthotolyl), 3-methylphenyl (metatolyl)}. However, 1:1 complexes of cadmium bromide could not be isolated. The infrared spectra of the ligands and the complexes were recorded on PerkinElmer 577 infrared spectrophotometer (200–4000 cm^{-1}) in CsI-supporting disc.

The crushed compound was loosely poured into a sample holder of Stanton-Redcroft TG 750 Thermobalance and, dispersed well. As efforts to minimize the local factors, only the freshly prepared samples were used and small sample size (4–8 mg) was taken in each case (to minimize the impact of heat and mass transfer phenomena). The thermograms were recorded keeping heating rate programmed at 10 K min^{-1} and using dry air as the purge gas. The residues were analysed for percentage of metals and halogens by dissolving them as usual.

Result and discussions

As expected, all the complexes were diamagnetic. Although the $\overline{\nu}_{M-P}$ frequencies could not be assigned with certainty as they were expected to fall beyond 200 cm^{-1} , the shift in the P–C stretching frequencies on the formation of complex suggests that the metal is coordinating through the P of the ligand molecule. The values 1450, 1410 and 1005 cm^{-1} , in PPh_3 shift to 1465, 1420 and 1015 cm^{-1} in $[Hg(PPh_3)_2Cl_2]$ and to 1460, 1412 and 1010 cm^{-1} in $[Hg(PPh_3)_2Br_2]$ (Table 1). Similarly, the $\overline{\nu}_{P-C}$ frequency values shifted in $[Hg(TOTP)_2Br_2]$ (1448, 1425 and 1010 cm^{-1}) and $[Cd(TOTP)_2Br_2]$ (1445, 1428 and 1010 cm^{-1}) from 1450, 1430 and 1020 cm^{-1}. A little change was observed in $[Cd(TOTP)_2I_2]$ as well. In cases of $[Cd(TMTP)_2Cl_2]$ and $[Cd(TMTP)_2Br_2]$, the values (1455, 1425 and 1015 cm^{-1}) and (1458, 1430 and 1020 cm^{-1}) were assigned to changed P–C vibrations (from 1450, 1428 and 1020 cm^{-1} in TMTP). The peak at 225 cm^{-1} in $[Hg(PPh_3)_2Cl_2]$ and at 260 cm^{-1} in $[Cd(TMTP)_2Cl_2]$are indicative of terminal M–Cl bonds. These values support complexation involving M–P bond, as these are lower than those occurring in metal halides [48]. The vibration of the substituent group in the ligand remains intact in its position even in the complex. The vibrations of the aromatic ring both in ligands and in their complexes for example, show that the ring is intact. 3–4 peaks (2880–2960 cm^{-1}) in the tolyl ligand move only slightly on complexation indicating that the methyl group remains intact in the side chain. Peaks in the ranges 670–735 cm^{-1} (P–Ph_3), 672–745 cm^{-1} (*o*-tolyl) and 680–785 cm^{-1} (*m*-tolyl) which are lowered by 5–10 cm^{-1} on complexation, have been assigned to C–H out of plane vibrations. Those at 1568–1575 cm^{-1} have been assigned to C=C stretching vibrations and 3015–3050 cm^{-1} to C–H stretching vibrations in the complexes. And, tetrahedral structure seems plausible in all the seven cases.

All the complexes are stable upto 210°C (Fig. 1). The TG data of the first step of decomposition were subjected to kinetic analysis in each case. In the initial analysis, the α–T plots of $[Cd(TOTP)_2Br_2]$, $[Cd(TMTP)_2Cl_2]$, $[Cd(TMTP)_2Br_2]$ and

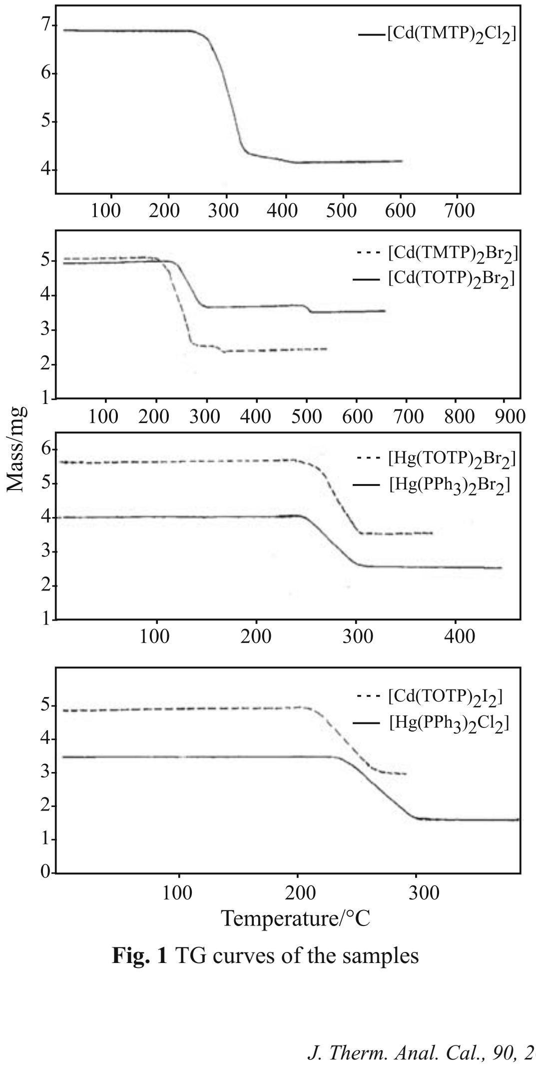

Fig. 1 TG curves of the samples

Table 1 Important IR frequencies and assignments

	Compounds	IR frequencies/cm^{-1}	Assignments
1	[Cd (TOTP)$_2$Br$_2$]	3020(s)[TOTP3020(s)]	C–H stretching
		2960–2880(m)(4 peaks) [TOTP2980–2900(w)(3 peaks)]	C–CH$_3$
		1562(s) [TOTP1570(s)]	C=C
		1445(s),1428(s),1010 [TOTP1450(s),1430(s),1020(s)]	P–C stretching
		1142(m),1050(w) [TOTP1145(s),1070(s)]	C–H in plane deformation
		735(s),700(s),650(v.w.) [TOTP745(s),705(s),672(s)]	C–H out of plane deformation
2	[Hg (TOTP)$_2$Br$_2$]	3020(s)	C–H stretching
		2980–2880(w)(3 peaks)	C–CH$_3$
		1568(s)	C=C
		1448(s),1425(s),1010 (s)	P–C stretching
		1140(s),1050(m)	C–H in plane deformation
		738(s),695(s),662(m)	C–H out of plane deformation
		230(s)	Hg–X
3	[Cd (TMTP)$_2$Cl$_2$]	2990(m)[TMTP3040(s),3020(s)]	C–H stretching
		2880 (m) [TMTP2960–2888 (s and w)(4 peaks)]	C–CH$_3$
		1570(s) [TMTP1568(s)]	C=C
		1455, 1425,1015(s) [TMTP1450(s), 1428(s),1020(s)]	P–C stretching
		1150(s),1080(s),1060(w) [TMTP1148(m),1080(s),1060(m)]	C–H in plane deformation
		760(s),672(s)[TMTP765(s),680(s)]	C–H out of plane deformation
		260(s)	Cd–Cl
4	[Cd (TMTP)$_2$Br$_2$]	3020(m)	C–H stretching
		2980(w),2890 (m)	C–CH$_3$
		1570(s)	C=C
		1458(s), 1430(m),1020(s)	P–C stretching
		1152(s),1090(s),1070(w)	C–H in plane deformation
		762(s),675(s)	C–H out of plane deformation
5	[Cd (TMTP)$_2$I$_2$]	3020(s)	C–H stretching
		2920(v.w.), 2890(s)	C–CH$_3$
		1570(s)	C=C
		1455(s), 1430(m),1030(s)	P–C stretching
		1155(s),1085(s),1065(m)	C–H in plane deformation
		770(s),672(s)	C–H out of plane deformation
6	[Hg (PPh$_3$)$_2$Cl$_2$]	3038(s)[PPh$_3$ 3015(s)]	C–H stretching
		1570(s),1555(w))[PPh$_3$1560(s)]	C=C
		1465(s),1420(s),1015(s) [PPh$_3$1450(s),1410(s),1005 (s)]	P–C stretching
		1085(s),1055(s)[PPh$_3$1068(s),1050(s)]	C–H in plane deformation
		735(s),703(s),682(s) [PPh$_3$735(s),720(s),700(s),670(s)]	C–H out of plane deformation
		225(s)	Hg–Cl vibrations
7	[Hg(PPh$_3$)$_2$Br$_2$]	3035(s)	C–H stretching
		1565(w),1550(w)	C=C
		1460(s),1412(s),1010 (s)	P–C stretching
		1080(s),1050(w)	C–H in plane deformation
		730(s),695(s),678(s)	C–H out of plane deformation

s=sharp; m=medium; w=weak; v.w=very weak

Table 2 The models followed and the parameters obtained

Sl. No.	Compound	Suggested mode of decomposition	Temp. range/ K	DTG peaks/ K	Best fitted mechanism	E_a/ kJ mol^{-1}	ln*A*	$\Delta S^{\#}$/ J K^{-1} mol^{-1}
1	$CdBr_2(TOTP)_2$	$CdBr_2(TOTP)_2 \rightarrow CdBr_2 \cdot TOTP$	483–703	512, 533, 558	4D diffusion	418.23	91.6	511.7
2	$CdCl_2(TMTP)_2$	$CdCl_2(TMTP)_2 \rightarrow CdCl \cdot TMTP$	513–693	533, 576, 635, 651	Second order	115	23.6	–54.15
3	$CdBr_2(TMTP)_2$	$CdBr_2(TMTP)_2 \rightarrow CdBr_2 \cdot TMTP$	500–578	543	3D diffusion	207.87	42.9	106.7
4	$CdI_2(TOTP)_2$	$CdI_2(TOTP)_2 \rightarrow CdI \cdot TOTP$	483–555	492, 523	4D diffusion	140.65	28	–16.8
5	$HgCl_2(PPh_3)_2$	$HgCl_2(PPh_3)_2 \rightarrow HgCl(PPh_3)_{0.5}$	513–593	534, 553	2D diffusion	170.21	34.6	37.63
6	$HgBr_2(PPh_3)_2$	$HgBr_2(PPh_3)_2 \rightarrow Hg \cdot PPh_3$	503–563	515, 542	Second order	226.82	51.7	180
7	$HgBr_2(TOTP)_2$	$HgBr_2(TOTP)_2 \rightarrow HgBr \cdot TOTP$	513–573	555	Contracting volume(R_3)	266.98	57	223.8

$[Hg(TOTP)_2Br_2]$ showed periods of induction (upto α~0.25, 0.053, 0.25 and 0.04 respectively) indicating that surface nucleation is taking place [49]. In other cases, the α *vs.* T curves present the well known sigmoidal shape of an autocatalytic process. The maximum $d\alpha/dt$ occurs at α~0.5 in all the cases. After this point, the curve presents a typical deceleratory behaviour and $d\alpha/dt$ decreases as the heating time increases.

Kinetic analysis of the TG data was carried out under linear temperature programming, and the values of ln*k* were calculated using various $f(\alpha)$ values [where $\ln k=\ln\{(d\alpha/dt)/f\alpha)\}$]. Spreadsheets [50] were prepared and the values of ln*A* and E_a were obtained from the most linear plot of ln*k* *vs.* $1/T$ using the following relation (regression analysis was carried out to test linearity):

$$\ln k=\ln A-E/RT$$

The values of $\Delta S^{\#}$ were approximated using the thermodynamic relation:

$$\Delta S^{\#}=R\ln Ah/kT$$

where $\Delta S^{\#}$=entropy of activation, R=gas constant, A=Arrhenius factor, k=Boltzman constant and T=time at α=0.5. The results have been put in Table 2. The compounds do not appear to be following any single kinetic model.

The following conclusions are drawn from the study:

- All the complexes are stable upto 210°C and $(d\alpha/dt)_{max}$ coincides with α~0.5 in all the cases.
- Complexation involving mercury brings better thermal stability than that with cadmium. The complexes containing Cl is more stable than that having Br. There is no change in thermal behaviour on changing the ligand from tri(2-methylphenyl)phosphane (TOTP) to tri(3-methylphenyl)phosphane (TMTP).
- Complexes having Br have higher E_a, ln*A* and $\Delta S^{\#}$ values than that having Cl.
- Changing the halogen from Cl to Br in $[Cd(TMTP)_2Cl_2]$ brings slight change in onset temperature which is accompanied by a sharp decrease in $\Delta S^{\#}$ value and decrease in E_a and ln*A* values.
- Diffusion seems to be more preferred path in the series.

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