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THERMAL STUDIES ON SOME BIOLOGICALLY ACTIVE ORGANOMERCURY(II) COMPLEXES*

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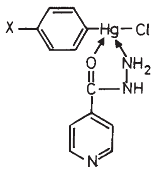
Abstract

Thermal behaviour of a number of organomercury(II) complexes of the type, *p*-$XC_6H_4HgCl(L^1)$ (I), *p*-$XC_6H_4HgCl_3(L^2)$ (II), *p*-$XC_6H_4HgL^3$ (III) and *p*-$XC_6H_4HgL^4$ (IV) [L^1=isoniazid, L^2=theobromine, L^3=phenyldithiocarbamate, L^4=*p*-nitrophenyldithiocarbamate; *X*=Me, MeO, NO_2] has been investigated. From TG curves, the order and activation energy of the thermal decomposition reaction have been elucidated. The variation of the activation energy has been correlated with the nature of the substituent on the phenyl ring. The heat of reaction has been elucidated from DSC or DTA studies. The fragmentation pattern has been analysed on the basis of mass spectra.

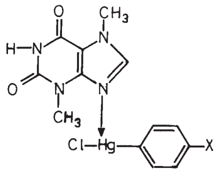
Keywords: biologically active material, kinetics, organomercury complexes

Introduction

Organomercury complexes are known to be potential diuretics, antiseptics, fungicides and bactericides [1]. We report here the thermal behaviour of a few organomercury(II) complexes with biologically active ligands (structures I–IV).



I.



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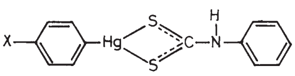

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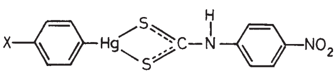

IV.

X = Me, MeO, NO_2

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This follows from our interest to investigate the thermal characteristics of organomercury-biomolecule interactions [2–5].

Experimental

Isoniazid and theobromine (Sigma) were used without further purification. Sodium dithiocarbamates were prepared by the method of Gilman and Blatt [6]. Arylmercury(II) chlorides (p-XC_6H_4HgCl, X= Me, MeO, NO_2) were synthesized by the literature method [7].

The isoniazid complexes were prepared by adding slowly a solution of p-XC_6H_4HgCl (0.01 mol) in 25 ml DMF to a stirred solution of isoniazid (0.01 mol) in 25 ml DMF. The contents were stirred for 6 h at 50°C and filtered. The filtrate was slowly poured over crushed ice and stirred vigorously. The precipitates so obtained were washed successively with hot water and benzene. The resulting product was dried and recrystallized from THF. The theobromine complexes were prepared by the same procedure. The dithiocarbamate complexes too were prepared similarly by the reaction of p-XC_6H_4HgCl and sodium dithiocarbamates.

The IR and UV spectra were recorded on Shimadzu model IR-435 and Perkin Elmer UV-Vis spectrometer model 554 respectively. The TG curves upto 1273 K and DSC/DTA curves upto 673 K were recorded on RIGAKU 8150 instrument in air atmosphere, at a heating rate of 15°C min^{-1}. Mass spectra were recorded on a Jeol JMX DX-303 spectrometer.

Results and discussion

In the IR spectra of isoniazid, the amide I (νCO) band occurred at 1660 cm^{-1}. In the complexes, the band shifted to ca. 1600 cm^{-1}. The ν(N–H) vibrations also shifted from 3300 cm^{-1} in the free ligand to ca. 3150 cm^{-1} in the complexes. The observations reveal that isoniazid ligand was coordinated to mercury(II) ion through carbonyl and hydrazinic groups [8]. In the UV spectra the π–π^* absorptions of the chromopheric C=O group absorbed at 266 nm (logε 6.8) in isoniazid and at ca. 278 nm (logε ca. 5.2) in the complexes, confirming the involvement of this group in complexation. The absorption due to the ν(C=N) stretching frequency was shifted from 1540 cm^{-1} in free theobromine to ca. 1525 cm^{-1} in the complexes. The ν(C=O) stretching frequency, however, remained unaltered. It was, therefore, concluded that theobromine coordinated to mercury(II) ion through N(9) [9]. The monodentate or bidentate behaviour of the dithiocarbamates is reflected in the ν(C$\overset{...}{=}$S) stretching frequency [10]. The presence of one band at ca. 1000 cm^{-1} reveals bidentate behaviour, a doublet being expected in case of monodentate behaviour. In the present complexes, only one absorption band at ca. 1000 cm^{-1} was observed in dithiocarbamate complexes, supporting the bidentate nature of the ligands. In the UV spectra, the ligand displayed a band at ca. 340 nm, attributed to π–π^* transition of S$\overset{...}{=}$C$\overset{...}{=}$S chromophore. This band tended to

Table 1 Thermal data

Compound	TG			DSC or DTA*		
	T_{range}	n	E_a/kcal mol^{-1}	Thermal effect	T_{max}/K	ΔH/ (muv^a min g^{-1}) or cal g^{-1*}
p-MeC$_6$H$_4$HgCl(L^1)	449–528	1	28.76	endothermic exothermic	501 512	664.72 647.28
p-MeOC$_6$H$_4$HgCl(L^1)	435–498	1	30.50	endothermic	490	529.89
p-NO$_2$C$_6$H$_4$HgCl(L^1)	470–573	1	27.44	exothermic exothermic	537 595	469.61 3307.57
p-MeC$_6$H$_4$HgCl(L^2)	436–673	1	21.34	exothermic endothermic	441 481	483.78 247.67
p-MeOC$_6$H$_4$HgCl(L^2)	498–643	1	22.88	exothermic endothermic exothermic	409 446 623	75.49 244.32 190.74
p-NO$_2$C$_6$H$_4$HgCl(L^2)	443–698	1	18.30	exothermic	598	110.64
p-MeC$_6$H$_4$HgL^3	382–614	1	12.20	endothermic	530	50.28*
p-MeC$_6$H$_4$HgL^3	499–565	1	21.73	endothermic	513	45.83*
p-NO$_2$C$_6$H$_4$HgL^3	388–613	1	6.30	endothermic	540	39.86*
p-MeC$_6$H$_4$HgL^4	458–578	1	9.15	endothermic	502	51.26*
p-MeOC$_6$H$_4$HgL^4	528–590	1	36.60	endothermic	568	43.61*
p-NO$_2$OC$_6$H$_4$HgL^4	510–623	1	8.69	endothermic	532	33.34*

[a] muv=micro unit volt

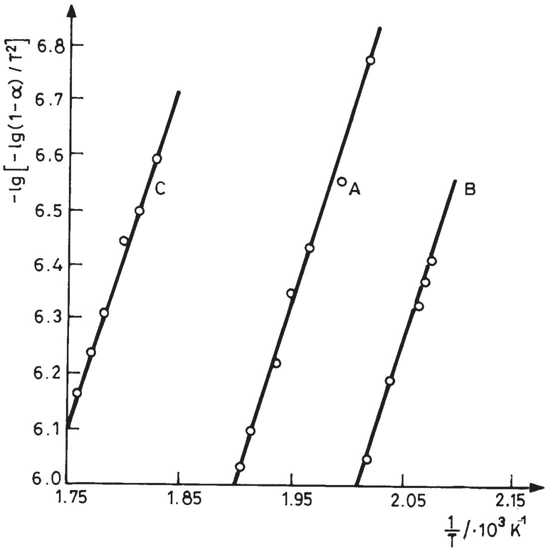

Fig. 1 Linearisation curves of isoniazid complexes: A – *p*-$MeC_6H_4HgCl(L^1)$; B – *p*-$MeOC_6H_4HgCl(L^1)$; C – *p*-$NO_2C_6H_4HgCl(L^1)$

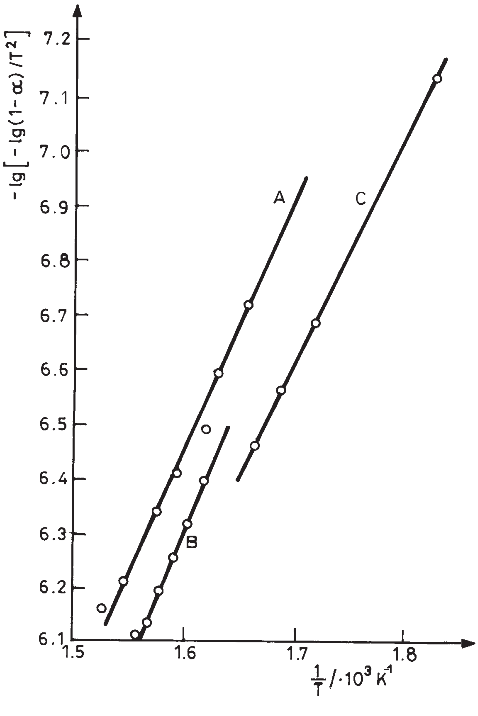

Fig. 2 Linearisation curves of theobromine complexes: A – *p*-$MeC_6H_4HgCl(L^2)$; B – *p*-$MeOC_6H_4HgCl(L^2)$; C – *p*-$NO_2C_6H_4HgCl(L^2)$

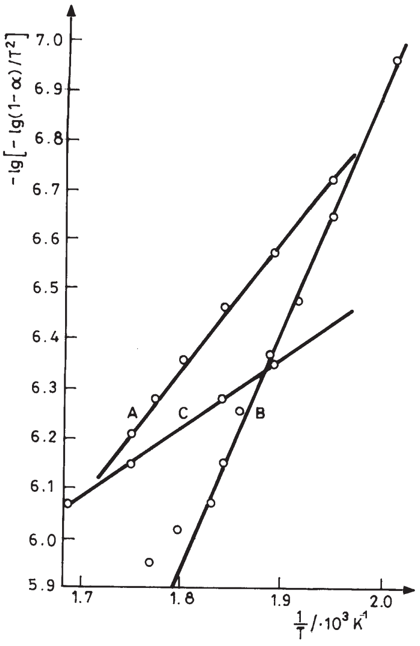

Fig. 3 Linearisation curves of phenyldithiocarbamate complexes: A – p-$MeC_6H_4HgL^3$; B – p-$MeOC_6H_4HgL^3$; (C) – p-$NO_2C_6H_4HgL^3$

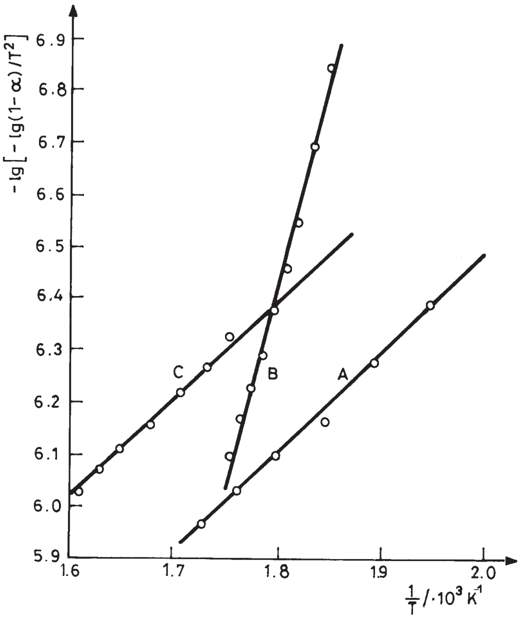

Fig. 4 Linearisation curves of p-nitrophenyldithiocarbamate complexes: A – p-$MeC_6H_4HgL^4$; B – p-$MeOC_6H_4HgL^4$; C – p-$NO_2C_6H_4HgL^4$

disappear in the complexes, confirming the conclusions of IR spectra that dithiocarbamates behave as bidentate ligands [11].

From TG curves, the mass loss accompanying the thermal degradation of the complexes has been calculated. In each case, the theoretical as well as calculated mass change corresponded to the formation of mercury(II) oxide. Beyond ca. 750 K, HgO slowly volatilised, leaving the crucible of the thermobalance vacant. The DSC/DTA profile showed, in each case, thermal effects, corresponding to the decomposition of the complex to HgO. Thermal data are presented in Table 1.

From the TG curves, the order (n) and activation energy (E_a) of the thermal decomposition reaction have been calculated by the method of Coats and Redfern [12]. The linearisation curves of the complexes I, II, III and IV are shown in Figs 1, 2, 3 and 4, respectively.

The order of reaction in each case is unity, similar to the lanthanide complexes reported by us recently [13]. A comparison of the activation energy data for each series of complexes revealed that the *p*-nitrophenylmercury(II) derivative had the lowest value of E_a. This may be explained on the basis of the electron withdrawing effect of the nitro group, which causes the weakening of the metal-ligand bond, consequently making thermal degradation relatively easy. In case of *p*-methylphenylmercury(II) analogue, the methyl group was of electron releasing type and the metal-ligand bond was strengthened, which subsequently resulted in higher E_a value for thermal reaction. As the methoxy group had a greater electron donating character than the methyl group, the *p*-methoxyphenylmercury(II) compound had the highest value of E_a. Thus for any one of the ligand, the activation energy varied in the order, X=MeO>O>Me>NO_2.

That the XC_6H_4–Hg bond cleavage was involved in the pyrolysis of the complexes was also evidenced from the mass spectra. The carbonium ion, $XC_6H_4^+$, constituted the base peak in each case. Thus the peaks at *m*/*e* 91, 107 and 122 corresponded to the formation of $MeC_6H_4^+$, $MeOC_6H_4^+$, and $NO_2C_6H_4^+$ fragments respectively. The mass spectra also showed peaks corresponding to $C_6^4H_4^+$ (*m*/*e* 76), $HgCl^+$ (*m*/*e* 236) and Hg^+ (*m*/*e* 201).

The TG data were supplemented by DSC/DTA studies. The heat of reaction (ΔH) was enumerated from DSC/DTA curves. For dithiocarbamate complexes, *p*-$XC_6H_4HgL^3$ and *p*-$XC_6H_4HgL^4$, the thermal effects on DTA curves were of endothermic nature. At least one exothermic thermal effect on DSC curves was recorded for the theobromine complexes, *p*-$XC_6H_4HgCl(L^2)$ and isoniazied complexes, *p*-$XC_6H_4Hg(L^1)$. However, no exothermic thermal effect was observed for the *p*-$MeOC_6H_4HgCl(L^1)$ complex. As these complexes had a chloro group in addition to the ligand moiety, it may be possible that the exothermic step in the thermal reaction involved the release of hydrogen chloride gas.

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