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Solid-state chemistry of new Tl_2OCl_2 and Tl_4Cl_6

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Solid thallous carbonate reacts with chlorine gas with the formation of brown-coloured Tl_2OCl_2 as an intermediate compound. Further exposure to chlorine gas gives the yellow compound Tl_4Cl_6. Both the compounds contain Tl(I) and Tl(III) ions. The kinetic data obey $w^2 = kt$. The energy of activation was found to be 41.98 kcal mol^{-1}. Thermogravimetry (TG) indicates that Tl_2OCl_2 decomposes into TlCl, Tl_2O_3 and chlorine gas above 250° C. In contrast, Tl_4Cl_6 is stable up to 420° C.

1. Introduction

Solid thallous carbonate reacts with bromine and iodine vapours [1, 2] forming compounds of the type Tl_2OX_2 (X = Br, I). During recent years solid-state reactions have been studied extensively because of their industrial importance [2]. Among the physical properties of solid materials which have been used as heterogeneous catalysts in a variety of chemical industries, the electrical conductivity and thermoelectric power are of great fundamental importance [3]. The electrical properties of catalysts are of basic importance in the determination of the relationship between the electronic structures and the catalytic properties of semiconductors. In this communication, we report the syntheses of Tl_2OCl_2 and Tl_4Cl_6 in solid-state and the characterization of both compounds by chemical analyses, X-ray diffraction patterns, thermal stability and kinetic measurements.

2. Material and experimental techniques

Thallous carbonate (BDH, England) was used without further purification. Chlorine gas was produced by the usual laboratory method. KCl and MnO_2 were mixed together and kept in a long-necked round-bottomed flask, and concentrated H_2SO_4 was added drop by drop. The gas evolved was passed through different absorbers to remove CO_2, oxygen gas and moisture. Alcoholic KOH was used for absorbing CO_2, pyrogallol solution was used for absorbing oxygen gas and silica gel was used for absorbing moisture.

Two experiments were carried out to prepare the reaction products. A known amount of Tl_2CO_3 was taken in a glass tube and dry chlorine gas was allowed to pass until the increase in weight of Tl_2CO_3 corresponded to the formation of Tl_2OCl_2 (brown colour). In a separate experiment a known amount of Tl_2CO_3 was taken in a glass tube and dry chlorine gas was allowed to pass until there was no increase in the weight of Tl_2CO_3. During the experiment, first a brown-coloured compound was formed and this was ultimately converted into yellow Tl_4Cl_6 compound.

The apparatus used for the study of the kinetics is shown in Fig. 1. One part of the assembly produces chlorine gas. This is connected to a glass bulb containing Tl_2CO_3 through a manometer. The addition of H_2SO_4 over a mixture of KCl and MnO_2 is regulated in such a way that the pressure of the gas remains constant during the course of the experiment. This was indicated by a constant level of the liquid (paraffin oil over mercury) in the manometer. The kinetics was followed by noting the increase in the weight of Tl_2CO_3 as a function of time. The experiment was carried out at 30, 40, 50, 60 and 70° C. The particle size was > 300 mesh. The results are given in Figs. 2 and 3.

Tl(I) and Tl(III) in Tl_2OCl_2 and Tl_4Cl_6 were estimated gravimetrically by the usual technique. The unreacted thallous carbonate was removed by washing the reaction product with water several times, and the excess chlorine gas was removed by washing with benzene. The product was dissolved in dilute HNO_3 and both Tl(I) and Tl(III) was precipitated as Tl_2CrO_4 by the

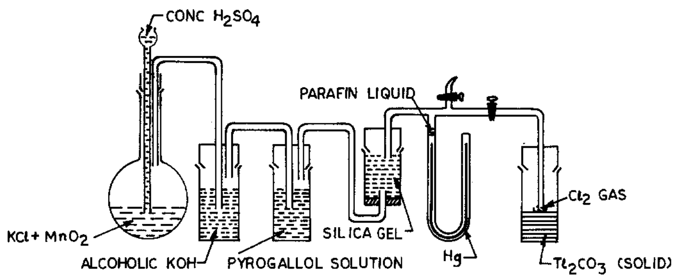

Figure 1 Apparatus for the study of kinetics of the reaction between Tl_2CO_3 (solid) and chlorine gas.

addition of potassium chromate solution. The precipitate was filtered and sulphurous acid was added to the filtrate to reduce Tl(III) to Tl(I). Tl(I) was precipitated as Tl_2CrO_4. The precipitates of Tl_2CrO_4 obtained in the two cases were dried and weighed. The results are given in Tables I and II.

The chloride ion content was estimated as silver chloride in the usual manner. The results are given in Tables I and II.

X-ray diffraction patterns of the reaction products were taken using Cu*Kα* radiation at 295 K. The X-ray diffraction pattern of Tl_2OCl_2 was taken with a vertical Guinier camera at Institute of Technology, Banaras Hindu University, whereas that of Tl_4Cl_6 was taken with a diffractograph at BRAC, Bombay. The results are given in Table III.

Thermal treatment of Tl_4Cl_6 shows that it melts at 430° C. When heated it in an electric furnace at a temperature > 430° C, brown-coloured liquid was obtained, which on cooling again converted into the yellow-coloured compound Tl_4Cl_6. The intermediate compound (Tl_2OCl_2) melts at 250° C, and on further heating it starts decomposing.

Thermogravimetry of Tl_2OCl_2 and Tl_4Cl_6 was carried out in the temperature range 40 to 660° C and 40 to 520° C, respectively, using a thermogravimetric analyser (Fertilizer Corporation of India Ltd, Sindri, India). The heating rate was 5° C min^{-1}. A platinum crucible was used. The results are given in Fig. 4.

The electrical conductivity σ and thermoelectric power S of pressed solid pellets of Tl_2OCl_2 and Tl_4Cl_6 were measured in the temperature range 300 to 580 K. The prepared specimens were pelletized at pressures $> 6 \times 10^6$ g cm^{-1} using a hand-operated hydraulic press and a suitable die. The pellets were annealed for a few hours at 500 K, cleaned, dried, and gently silver painted on two faces before being placed into a specially designed sample holder described elsewhere [4]. The details of our experimental techniques for both electrical conductivity and thermoelectric

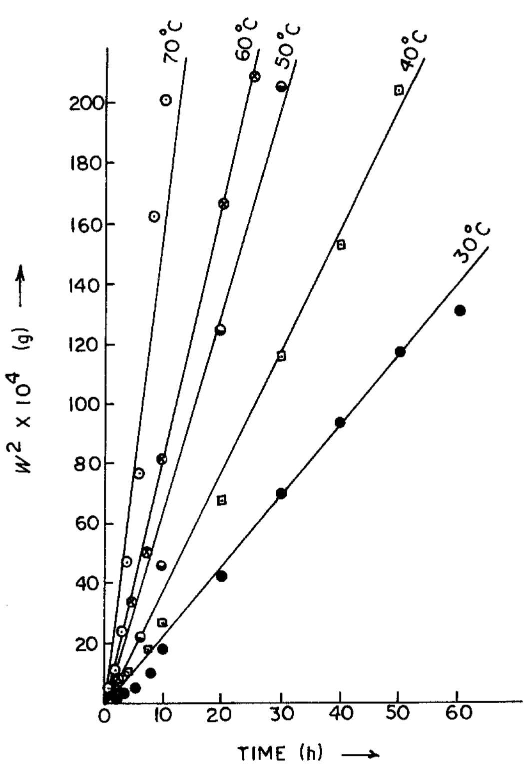

Figure 2 Kinetic data for the reaction between Tl_2CO_3 (solid) and chlorine gas (particle size > 300 mesh).

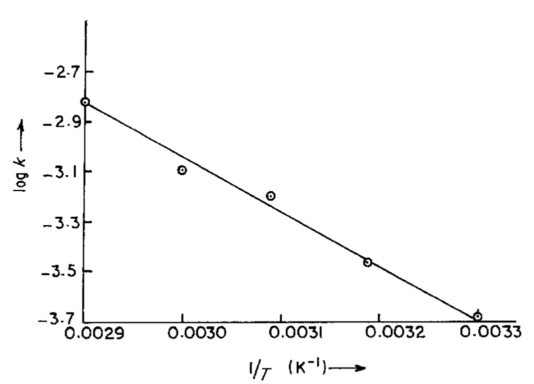

Figure 3 Effect of temperature on k for reaction between Tl_2CO_3 (solid) and chlorine gas.

TABLE I Chemical analyses data for Tl(I), Tl(III) and Cl^- ion in the reaction product Tl_2OCl_2

Weight of Tl_2OCl_2 (g)	Weight of Tl_2CrO_4 (g)	Percentage of Tl(I)		Weight of Tl_2CrO_4 obtained after reduction (g)	Percentage of Tl(III)		Weight of Tl_2OCl_2 (g)	Weight of AgCl (g)	Percentage of chlorine	
		Observed	Calculated		Observed	Calculated			Observed	Calculated*
1.0060	0.5410	41.13	41.22	0.5298	41.26	41.22	1.0234	0.5900	14.59	14.32
1.0042	0.5300	41.28	41.22	0.5304	41.19	41.22	1.0012	0.5812	14.28	14.32
1.0016	0.5314	41.19	41.22	0.5288	41.18	41.22	1.0074	0.5850	14.27	14.32

*Calculated from the formula Tl_2OCl_2.

TABLE II Chemical analyses data for Tl(I), Tl(III) and Cl^- ion in the reaction product Tl_4Cl_6

Weight of Tl_4Cl_6 (g)	Weight of Tl_2CrO_4 (g)	Percentage of Tl(I)		Weight of Tl_2CrO_4 obtained after reduction (g)	Percentage of Tl(III)		Weight of Tl_4Cl_6 (g)	Weight of AgCl (g)	Percentage of chlorine	
		Observed	Calculated		Observed	Calculated			Observed	Calculated*
1.0004	0.7588	59.10	59.51	0.2442	19.02	19.84	1.0020	0.8572	20.71	20.67
1.0040	0.7492	58.40	59.51	0.2586	20.10	19.84	1.0008	0.8296	20.54	20.67
1.0026	0.7616	59.32	59.51	0.2496	19.42	19.84	1.0062	0.8402	20.68	20.67

*Calculated from the product $Tl_3[TlCl_6]$.

TABLE III X-ray diffraction pattern for the compounds Tl_2OCl_2, Tl_4Cl_6, Tl_2O_3 and Tl_2CO_3

Tl_2OCl_2		Tl_4Cl_6		Tl_2O_3			Tl_2CO_3	
d (nm)	I/I_0	d (nm)	I/I_0	d (reported) (nm)	I/I_0	d (observed) (nm)	d (nm)	I/I_0
0.47446	32	0.4725	vw	0.3042	100	0.3042	0.557	5
0.40629	70	0.4062	w	0.2816	30	0.2818	0.485	5
0.38986	100	0.3875	mw	0.2635	42	0.2636		
0.37263	80	0.3723	w	0.2484	20	0.2480	0.441	80
0.34755	25	0.3636	s	0.2357	25	0.2360	0.400	30
0.31872	40	0.3473	s	0.2248	30	0.2250	0.330	20
0.27306	20	0.3194	vw	0.2149	20	–	0.314	20
0.26823	23	0.2730	s	0.2068	22	–	0.307	30
0.26076	50	0.2669	s	0.1924	26	0.1930	0.297	100
0.24945	40	0.2607	mw	0.1863	33	0.1860	0.276	5
0.22762	26	0.2486	mw	0.1808	26	–	0.246	20
0.21218	28	0.2276	m	0.1758	18	–	0.245	30
0.20581	30	0.2122	m	0.1710	20	0.1720	0.220	20
0.18875	43	0.2059	ms	0.1587	27	0.1560	0.201	10
0.18375	32	0.1887	w					
0.18105	20	0.1837	mw					
0.17524	38	0.1811	vvs					
		0.1753	vs					
		0.1613	s					
		0.1473	m					
		0.1359	mw					

Key: w = weak, s = strong, v = very.

power measurements have already been described in an earlier publication [5]. The conductivity measurements were more accurate with typical errors remaining less than two per cent at all temperatures.

3. Results and discussion

The kinetic studies indicate that as soon as chlorine gas comes into contact with thallous carbonate, a rapid reaction, with the formation of a brown-coloured intermediate compound, is formed which further reacts with chlorine gas to give a yellow-coloured compound. The overall rate of the reaction is expressed by the equation

$$w^2 = kt \quad (1)$$

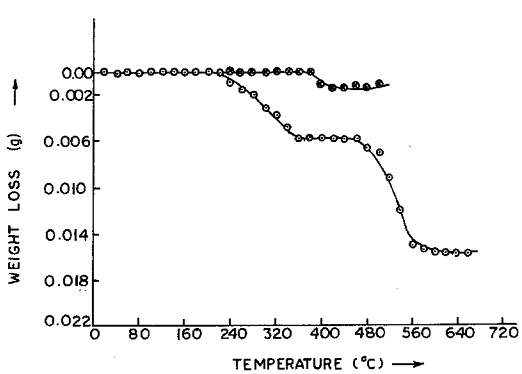

Figure 4 TG data of Tl_2OCl_2 (⊙) and Tl_4Cl_6 (⊗).

where w is the change in weight at any time t and k is the rate constant. A plot of w^2 against t, gives a straight line (see Fig. 2). The values of k at different temperatures are calculated, and from this it is clear that the rate of reaction increases with the rise in the temperature. The plot of log k against $1/t$ gives a straight line (see Fig. 3), showing that the Arrhenius equation is obeyed. From the slope of the curve (see Fig. 3), the energy of activation was evaluated and found to be 41.98 $kJ\ mol^{-1}$ (10.03 $kcal\ mol^{-1}$). First of all a reaction product is formed which blocks the passage of the diffusion of chlorine molecules. Since the reaction proceeds to completion and the energy of activation is very low, it appears that some type of crack or easier path is created in the product layer and diffusion continues till the completion of the reaction.

The X-ray diffraction patterns of both Tl_2OCl_2 and Tl_4Cl_6 (see Table III) indicated that the diffraction lines corresponding to those of Tl_2CO_3, $TlCl$, $TlCl_3$, Tl_2O and Tl_2O_3 were absent. From this it is concluded that the final reaction products were a single-phased Tl_2OCl_2 and Tl_4Cl_6. The stoichiometry of the reactions indicates the possibility of the following reactions:

$$Tl_2CO_3 + Cl_2 \longrightarrow Tl_2OCl_2 + CO_2 \quad (2)$$

$$2Tl_2OCl_2 + Cl_2 \longrightarrow Tl_4Cl_6 + O_2 \quad (3)$$

The product, Tl_2OCl_2, of Equation 2 is brown, gives a negative test for carbonate and a positive test for oxygen. Further the theoretical amounts of Tl(I), Tl(III), and Cl^- ions in Tl_2OCl_2 correspond to the values observed given in Table I.

The final product is the product of Equation 3. Tl_4Cl_6 is yellow. It contains both Tl(I) and Tl(III) ions. The theoretical amounts of Tl(I), Tl(III) and Cl^- ions in the compound correspond to the values observed given in Table II.

On the basis of the qualitative and quantitative chemical analyses the compound Tl_2OCl_2 can be represented as $Tl^{I}[Tl^{III}OCl_2]$ whereas the compound Tl_4Cl_6 can be represented by either one of the following formulae: $TlCl_3$–3TlCl or $Tl^{I}_3[Tl^{III}Cl_6]$.

When Tl_2OCl_2 was heated at a temperature > 250° C it started decomposing. Some of the products of the decomposition were tested qualitatively and were found to be TlCl, chlorine gas and oxygen gas. Thermogravimetry studies (see Fig. 4) indicate that the compound, Tl_2OCl_2, may decompose in the following manner:

$$4Tl_2OCl_2 \longrightarrow 6TlCl + 2TlOCl + O_2 \quad (4)$$

$$2TlOCl + O_2 \longrightarrow Tl_2O_3 + Cl_2 + \tfrac{1}{2}O_2 \quad (5)$$

The second step of decomposition, i.e. Equation 5, may consist of the following reaction:

$$2TlOCl \longrightarrow Tl_2O + Cl_2 + \tfrac{1}{2}O_2 \quad (6)$$

and the product Tl_2O may immediately combine with the atmospheric oxygen and convert into Tl_2O_3:

$$Tl_2O + O_2 \longrightarrow Tl_2O_3 \quad (7)$$

Since Tl_2O is stable only up to 300° C, and above that it is immediately converted into Tl_2O_3 [6], it is not indicated in the thermogravimetry curve.

The final yellow product, Tl_4Cl_6, when heated at a temperature above 430° C, melted and converted into brown liquid, which on cooling was again converted to a yellow solid. Thermogravimetry data (Fig. 4) indicates that there is no weight loss up to 420° C, indicating that Tl_4Cl_6 is stable up to 420° C.

The electrical conductivity and thermoelectric power of these compounds have been measured in the temperature range 300 to 580 K. The value of conductivity of Tl_2OCl_2 lies in the range 0.95×10^{-3} to 0.42×10^{-1} ohm^{-1} cm^{-1} and for Tl_4Cl_6 0.52×10^{-8} to 0.73×10^{-4} ohm cm^{-1} for the temperature range 300 to 580 K. It seems that both Tl_2OCl_2 and Tl_4Cl_6 are semiconductors. Thermoelectric power measurements show that in both Tl_2OCl_2 and Tl_4Cl_6, the elelectrons are the charge carriers. Details of the electrical transport studies will be reported shortly.

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