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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. XXVI

DSC study on the thermal decomposition of some metal and ammonium salts of the acid hydrogen hexachlororhenate(IV)

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Ten metal and ammonium salts of the acid $H_2[ReCl_6]$ were obtained by double decomposition reactions, and their pyrolyses in air atmosphere were studied by means of DSC measurements. The kinetic parameters of these reactions were derived and are discussed.

Rhenium forms mono- and binuclear halogeno and oxyhalogeno acids of different types, depending on the nature of the halogen and the oxidation state of the metal. The acids $HReX_4$ and H_3ReX_6, containing Re(III), are not stable and are easily transformed into other products. After the perrhenates (Re(VII)), the Re(IV) derivatives are the most stable. Tme hexachloro derivatives of the type $M_2[ReCl_6]$ can readily be obtained from metallic Re and gaseous chlorine in the presence of alkali metal chlorides [1]. The salts $M_2[ReBr_6]$ and $M_2[ReI_6]$ are formed by the reduction of $MReO_4$ in the presence of HBr and HI, respectively [2–3].

The corresponding free acids are weak dibasic acids and give metal and metal(III)-amine salts of various types (e.g. $[Co(NH_3)_5Y][ReX_6]$, $[Co(en)_2Y_2]_2[ReX_6]$, $[Co(DH)_2(amine)_2]_2[ReX_6]$, etc. [4–5]). In acid media they also form a series of ammonium and phosphonium salts with aliphatic, aromatic and heterocyclic N-bases and tertiary phosphines [6–8].

The thermal decomposition of some $(amine \cdot H)_2[ReX_6]$ complexes was studied by Tronev et al. [9–11]. In inert gas atmosphere the formation of tetrahalogeno intermediates has been reported to occur according to the equation:

$$(amine \cdot H)_2[ReX_6] = [Re(amine)_2X_4] + 2\ HX \qquad (1)$$

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The liberation of the hydrogen halides is an endothermal process, as observed by Chatt and Rowe [12] in the pyrolysis of the analogous phosphine derivatives $(HPR_3)_2[ReX_6]$.

Hydrogen chloride is also evolved when some ammonium salts of the oxo-chloro acids of pentavalent rhenium are heated [13]:

$$(\text{amine}\cdot H)_2[ReOCl_5] = [Re(\text{amine})_2OCl_3] + 2\ HCl \qquad (2)$$

Results and discussion

In the present paper, 10 hexachlororhenates(IV) were obtained by double decomposition reactions from $K_2[ReCl_6]$ with metal chlorides and with hydrochlorides of some aromatic and heterocyclic amines. The studied complexes are characterized in Table 1.

Table 1 Analytical data on the M_2ReCl_6 type complex salts

No.	Formula	Appearance		Analysis	
				calcd.	found
1	Ag_2ReCl_6	orange yellow microcryst.	Ag Re	35.10 30.29	35.97 31.00
2	Hg_2ReCl_6	orange yellow microcryst.	Re	23.27	23.70
3	Tl_2ReCl_6	orange cryst. crops	Tl Re	52.60 23.05	52.10 22.45
4	$(NH_4)_2ReCl_6$	green-yellow irregular cryst.	Re	42.80	42.46
5	$(py\cdot H)_2ReCl_6$	green-yellow irregular cryst.	Re N	33.30 5.01	32.70 4.75
6	$(\beta\text{-pic}\cdot H)_2ReCl_6$	yellow prisms	Re	31.72	31.45
7	$(\gamma\text{-pic}\cdot H)_2ReCl_6$	yellow prisms	Re	31.72	32.15
8	$(3,5\text{-lut}\cdot H)_2ReCl_6$	yellow irregular cryst.	Re N	30.28 4.55	29.87 4.84
9	$(\text{benzimidazole}\cdot H)_2ReCl_6\cdot 2H_2O$	yellow irregular crops	Re	27.18	27.29
10	$(\text{oxin}\cdot H)_2ReCl_6\cdot 2H_2O$	yellow needles	Re N	25.61 3.85	25.45 4.14

The thermal decompositions of hexachlororhenates(IV) were studied by means of DSC.

The DSC measurements showed that all the studied substances were practically completely volatilized up to about 400–500°, with the exception of the silver salt, which is transformed into AgCl, with a very high boiling point. The volatility is not surprising, since all the heterocyclic N-bases used, as well as the oxides, chlorides and oxychlorides of rhenium, have boiling points below 400°, and further the chlorides of Hg(I) and Tl(I) are volatile.

The results of the DSC measurements are given in Table 2.

This Table lists the molar weights of the complexes studied, the DTA peak temperature for each thermal decomposition stage, the indication of the exothermic or endothermic character, the weight loss expressed in molar weight units, the overall weight loss in molar weight units and in percentage, and the temperature at which the final weight is reached.

Of the complexes studied, only the benzimidazole and the 8-hydroxyquinoline (oxine) derivatives contain crystallization water. The water molecules must be linked to the cations through hydrogen-bridges. For these complexes, the first decomposition stage is the endothermic release of the crystallization water; this occurs at lower temperatures for benzimidazole than for oxine, since the N—H...O bond is weaker than the O—H...O one.

The pyrolysis of the metal salts reflects the polarizing effect of the cations. In the case of Hg_2^{2+}, the decomposition begins at very low temperatures and is an exothermic process. The silver complex decomposes at higher temperatures, the pyrolysis also being exothermic. The thallium salt is the most stable and all the decomposition stages are endothermic ones.

The final weight of the sample is reached only at a relatively high temperature, which is nevertheless more than a hundred degrees lower than the boiling point of TlCl. It is worth mentioning that the silver complex gives a sharp endothermic peak, without weight loss, at 455°, corresponding to the melting point of AgCl. This indicates that the final product is AgCl. The weight loss observed is in agreement with this conclusion. The ammonium salt is the most stable of all the complexes studied. At first sight, its thermal decomposition seems to occur in a single exothermic stage, but before the clear exothermic peak at 365°, a not well-defined endothermic peak appears at about 300°. The weight loss occurring between 270 and 430° presumably begins with an endothermic decomposition reaction, but this is transformed into a more complicated, exothermic process, with the participation of atmospheric oxygen. The DTA curve has an asymmetric shape, for a shoulder appears on the high-temperature side, which is in agreement with the above hypothesis.

The onium salts of the heterocyclic N-bases begin their decomposition in a very

Table 2 Characteristics of the pyrolysis processes

No.	Compounds	M	Stage	1	2	3	4	5	6	7	$\Sigma\Delta M$	%	Final weight, T, °C
1	Ag_2A	614.6	DTA	215E	275E						313.5	51.0	300
			ΔM	92.2	221.3								
2	Hg_2A	800.1	DTA	95E	145E	275E	350*				696.0	84.5	415
			ΔM	8.0	20.0	504	164						
3	Tl_2A	807.6	DTA	342e	430e	530e					783.3	97.0	575
			ΔM	121	577.5	84.8							
4	$(NH_4)_2A$	434.9	DTA	365E							432.7	99.5	385
			ΔM	432.7									
5	$(pyH)_2A$	558.9	DTA	205e	270e	355E	410E				544.9	97.5	460
			ΔM	50.3	103.4	78.2	313						
6	$(\beta\text{-picH})_2A$	586.9	DTA	190e	265e	300E	330e	355E	410E	440E	570.5	96.0	410
			ΔM	20.5	102.7	123.2	70.4	246.5	4.7	2.5			
7	$(\gamma\text{-picH})_2A$	586.9	DTA	205e	285e	365e					578.1	98.5	360
			ΔM	70.4	255.3	252.4							
8	$(lutH)_2A$	614.9	DTA	185e	230e	275e	295E	365E	430E		606.3	98.8	450
			ΔM	12.3	55.3	89.2	58.4	246	145.1				
9	$(benzH)_2A \cdot 2H_2O$	684.9	DTA	85e	215e	275e	300e	340e	390E	405e	650.6	95.0	420
			ΔM	34.2	21.2	24.0	30.1	51.4	441.8	47.9			
10	$(oxinH)_2A \cdot 2H_2O$	726.9	DTA	110e	205e	270e	390E	435E	510E		705.1	96.8	520
			ΔM	34.2	105.4	58.2	14.5	72.7	420.1				

E – exothermic, e – endothermic, * – DTG peak temperatures, py – pyridine, pic – picoline, lut – 3,5-lutidine, benz – benzimidazole, oxin – 8-oxy-chinolein, A – $[ReCl_6]^{2-}$

narrow temperature interval. The first DTA peak is endothermic; it is situated between 185 and 215° for all six complexes studied. This first stage might be the reaction (1), found by Tronev et al. in inert gas atmosphere [10–11]. The weight loss in the first stage is in good agreement with this hypothesis only for the γ-picoline derivative. However, the weight losses in the first stage or in the first 2–3 stages are not in contradiction with reaction (1), except for the oxine derivative. It is interesting that, with the oxine derivative, the first weight loss after the dehydration corresponds to the release of three HCl molecules. The next endothermic peak appears near to the boiling point of oxine. The weight loss in this stage, together with the weight losses in the next two exothermal stages, corresponds to one oxine molecule. The last weight loss occurs at higher temperature than in the case of the other N-base derivatives, and corresponds to $Re(Ox)Cl_3$.

These phenomena suggest the idea that in the first stage an oxine molecule enters the inner coordination sphere of the Re and behaves as a bidentate ligand:

$$(OxH_2)_2[ReCl_6] = [Re(Ox)Cl_3] + OxH + 3\ HCl \tag{3}$$

where OxH stands for the oxine molecule.

The HCl molecules are evolved. At higher temperatures the oxine liberated earlier is volatilized and the presumed $[Re(Ox)Cl_3]$ remains; this might have a higher thermal stability than that of the complexes of type $[Re(amine)_2Cl_4]$.

Table 3 Kinetic parameters of some decomposition stages

Compound	Stage	τ^*	n	E, kJ/mole	$\log Z$
1	1	2.186	−0.74	34.7	0.55
1	2	1.919	0.74	151	12.1
2	3	2.061	0.33	90.9	6.71
3	1	1.689	0.01	158	11.2
3	2	1.457	0.02	76.5	2.37
4	1	1.663	2.03	155	10.4
5	4	1.486	0.70	181	11.0
6	5	1.639	1.03	361	28.0
7	3	1.664	−0.21	164	11.2
8	5	1.623	−0.05	255	18.6
8	6	1.505	0.89	197	12.6
9	1	3.060	0.84	112	15.4
9	2	2.066	1.02	602	62.5
9	6	1.612	0.94	207	14.3
10	1	2.880	1.23	146	19.5
10	2	2.147	0.17	198	20.3
10	6	1.335	0.59	268	15.6

The shape of the TG curves allowed us to derive kinetic parameters for some of the decomposition stages. For this purpose our nomogram method was used [15, 16]. Results are given in Table 3.

In this Table τ^* is the reduced position parameter, representing the corrected value of $\tau = 10^3 \cdot T_{0.1}$, where $T_{0.1}$ is the temperature at which the transformation degree is 10%. n, E and Z are the apparent reaction order, activation energy and pre-exponential factor, respectively, the last one expressed in s^{-1}.

It is seen that the values obtained are rather scattered and no clear conclusions can be drawn.

In the plot of log Z *vs.* E, the experimental points are also scattered. Via linear regression, values of $a = 0.089$ and $b = -0.83$ were obtained for the parameters of the linear compensation law

$$\log Z = aE + b \tag{4}$$

with a correlation coefficient of only $\varrho = 0.885$.

The quite bad linearity might be a consequence of the different character of the pyrolysis stages, the dehydration, the evolution of HCl, the evolution and/or oxidation of N-bases, and the evolution of TlCl, Hg_2Cl_2, and presumably of $ReCl_3$, ReO_3Cl, $ReOCl_4$, etc., occurring in a large temperature interval.

According to Garn [17], relation (4) is a consequence of the existence of an isokinetic temperature (T_c) and the coefficient a means

$$a = \frac{1}{2.3RT_c} \tag{5}$$

In order to verify Garn's hypothesis, the E and $\log Z$ data were processed separately for different temperature intervals. The results are given in Table 4.

In this Table, a^* was calculated by means of relation (5), taking the mean value of $T_{0.1}$ for T_c.

It may be seen from Table 4 that Garn's hypothesis is approximately valid. The differences between a^* and a are appreciable only if the temperature interval is wide and the number of experimental points is small.

Table 4 Compensation parameters for different decomposition temperature intervals

$T_{0.1}$, °C interval	nr exp. points	a^* mole/kJ	a mole/kJ	b	ϱ
54–184	3	0.1415	0.1743	−5.20	0.996
184–248	5	0.1084	0.1093	−3.08	0.999
319–413	9	0.0832	0.0878	−3.83	0.994
400–476	3	0.0745	0.0699	−2.56	0.993

Experimental

Syntheses: $K_2[ReCl_6]$: A mixture of 2 g metallic rhenium and 3 g KCl was heated in a glass tube at 250–300° in a slow stream of chlorine for 2–3 hours. The reaction product was dissolved in 50–60 ml water on a water bath, 6 g KCl was added and the mixture was cooled. After standing for 12–24 hours, the green-yellow crystalline product obtained was filtered off, washed with ice-cooled water and dried in the air.

$M_2[ReCl_6]$ and (amine H)$_2$[ReCl$_6$]: 10 mmoles of the chlorides or nitrates of the corresponding metals was dissolved in 25–30 ml water and treated with 1 mmole of $K_2[ReCl_6]$ in 10 ml aqueous solution. The crystalline products formed were filtered off, washed with water and dried in the air. The ammonium salts were obtained in an analogous way by treating 10 mmoles of amine with 1–1.5 ml conc. HCl on a water bath. The hydrochloride of the amine was dissolved in 25–30 ml water and treated with 1 mmole of $K_2[ReCl_6]$.

Analysis; The rhenium content was determined spectrophotometrically with furyldioxime [14].

Differential scanning calorimetric measurements

The measurements were carried out with a DuPont 990 Thermal Analyser (910 type DSC).

Heating rate: 5 deg/min, sample weight: 5–6 mg.

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Zusammenfassung — 10 Metall- und Ammoniumsalze der Säure $H_2[ReCl_6]$ wurden durch Doppelzersetzungsreaktionen erhalten. Die Pyrolyse dieser Salze in Luft wurde mittels DSC untersucht. Die kinetischen Parameter dieser Reaktionen wurden ermittelt und diskutiert.

Резюме — Реакцией двойного разложения получено десять металлических и аммониевых солей кислоты $H_2[ReCl_6]$. Методом ДСК в атмосфере кислорода изучен пиролиз этих солей. Установлены и обсуждены кинетические параметры реакций пиролиза.