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STUDY OF THE THERMAL DECOMPOSITIONS OF SOME TRANSITION METAL PERCHLORATES

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The thermal decompositions of nickel(II), copper(II), cobalt(II) and manganese(II) perchlorates were studied by thermal analysis and kinetic measurements. Anhydrous perchlorates could not be prepared by heating and outgassing the samples in vacuum; oxides were obtained as the main solid decomposition products. In the case of cobalt and manganese perchlorates, oxidation of the metal ions was observed during the decomposition. In most cases the decompositions of the perchlorates followed the Avrami-Erofeyev kinetics. A correlation was found between the stabilities of the perchlorates and the effective field strengths of the cations.

Of the salts of the oxyacids of chlorine, the metal perchlorates in particular have increased in importance during the past few decades. These compounds are used as the oxygen source of solid rocket propellants, this being the primary factor in making the study of their thermal stabilities a topical question. Up to the present, however, detailed measurements have been made only on the alkali metal and alkaline earth metal perchlorates [1, 2]. Reliable data are available on the physicochemical properties of these compounds, and the regularities and probable mechanisms of their thermal decompositions are known. In contrast, data relating to the thermal stabilities of the transition metal perchlorates are very scarce, only a few investigations of an informatory nature having been published, in the first half of this century [3—7]. The majority of the experimental work relates to the preparation of the compounds, and to establishment of the compositions of the hydrates.

For a deeper understanding of the effects of various transition metal oxides on the decomposition of perchloric acid, it appeared necessary to carry out a detailed study of the stabilities of the transition metal perchlorates, and the characteristics of their decompositions. It seemed probable that the decomposition of perchloric acid proceeds via formation and decomposition of surface perchlorate on the oxides, and thus the thermal stabilities of the transitionally-formed metal perchlorates play a significant role in the effectivities of the oxides and in the courses of the catalytic reactions [8—11]. The present paper reports experiments with copper(II), nickel(II), cobalt(II) and manganese(II) perchlorates. Although the primary aim of the work was to study the irreversible decompositions of the perchlorates, measurements were also made with regard to the dehydration of perchlorates containing crystal water, and the preparation of the anhydrous salts. After the completion of our experiments and the utilization of the main results in the study of the catalytic decomposition of perchloric acid and in the establishment of the mechanism of the catalytic reaction [8–11], Vilcu and Georgescu [12] published a paper on the decompositions of the transition metal perchlorates. Their experimental results differ considerably from those reported here, and we deal with them in a later part of this paper.

Experimental

Materials

Copper(II) perchlorate: Copper(II) hydroxide, freshly prepared from p.a. $Cu(NO_3)_2$ and 25% NH_4OH and thoroughly washed, was added to the calculated amount of 60% $HClO_4$. The solution was concentrated on a water-bath. Composition of the material obtained on crystallization: $Cu(ClO_4)_2 \cdot 6H_2O$.

Nickel(II) perchlorate: The calculated amount of p.a. $NiCO_3$ was added to 70% $HClO_4$. The solution was concentrated by careful heating on a water-bath. The crystals precipitating after cooling of the solution were separated from the mother liquor by filtration, and then dried in vacuum. Composition of the compound: $Ni(ClO_4)_2 \cdot 6H_2O$

Cobalt(II) perchlorate: The calculated amount of $CoCO_3$ was added to 7% p.a. $HClO_4$. The solution was clarified by careful heating on a water-bath, and on further heating small red crystals precipitated. These were filtered off, dried in a vacuum desiccator and stored. Composition: $Co(ClO_4)_2 \cdot 6H_2O$.

Manganese(II) perchlorate: A saturated solution of barium perchlorate was added during stirring to a cold concentrated solution of manganese(II) sulphate. The barium sulphate was removed by filtration. The crystals precipitating from the filtrate were dried in vacuum. Composition: $Mn(ClO_4)_2 \cdot 6H_2O$.

Measurements

The perchlorates were subjected to thermal analysis in a stream of nitrogen in a MOM derivatograph, or in vacuum in a microbalance. Kinetic measurements were made under isothermal conditions in vacuum, by simultaneous measurement of the weight change and the pressure of oxygen released. Chlorine and chlorine dioxide were frozen out in a vessel cooled with liquid air. The microbalance and the experimental method were described in detail earlier [13, 14].

Infrared studies were performed with a Spektromom 2000 infrared spectrometer.

Results

Copper(II) perchlorate

Thermoanalytical studies

The thermoanalytical curves of $Cu(ClO_4)_2 \cdot 6H_2O$ are shown in Fig. 1. The weight begins to decrease at 100–120°. Endothermic peaks are found at 71, 153, 240 and 300°. The first of these is in all probability the result of a modification change, since it is not accompanied by a weight change. The sharp peaks at 290, 310 and 328° in the DTG curve demonstrate the decomposition of the compound in several steps. The weight of the residue from total decomposition shows the weight loss to be 78.69 %, of which 29.1 % is due to the loss of the 6 molecules of crystal water. This weight loss is indicative of the following decomposition equation:

$$Cu(ClO_4)_2 \cdot 6H_2O = CuO + Cl_2 + 3.5O_2 + 6H_2O \qquad (1)$$

With the aim of separating the dehydration and the irreversible decomposition, the decomposition of the compound was also studied in vacuum, at a heating rate of 2.5°/min. The results are presented in Fig. 2.

The curve shows that the compound loses its crystal water in two steps between 90 and 210°; the weight loss is 33.2 %. No gas evolution can be observed in this stage. The theoretical weight loss is 29.1 %. A further slight decrease in weight occurs up to 250°, above which there is a rapid weight loss, indicative of considerable irreversible decomposition. Oxygen evolution begins then too.

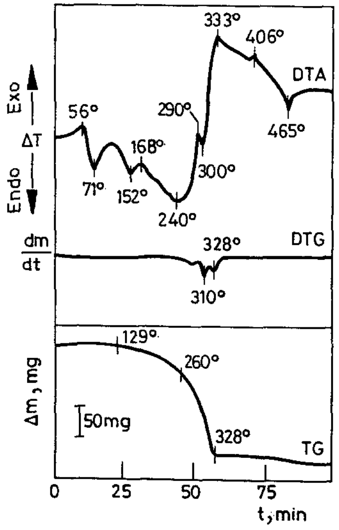

Fig. 1. DTG, DTA and TG curves for the thermal decomposition of $Cu(ClO_4)_2 \cdot 6 H_2O$ in air. Heating rate: 6°/min, sample weight: 260 mg

In the following experimental series, 45 mg samples of $Cu(ClO_4)_2 \cdot 6H_2O$ were maintained under constant suction in vacuum at 100, 140, 180, 220 and 260°. A sample was heated to higher temperature only when the weight of the material no longer changed at the lower temperature. The results are depicted in Fig. 3.

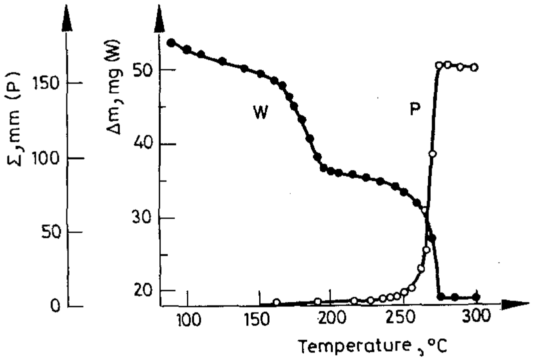

Fig. 2. Decomposition of $Cu(ClO_4)_2 \cdot 6\,H_2O$ in vacuum. Heating rate: 2.5°/min. *W*: weight change, *P*: pressure of oxygen evolved, in oil-millimetres (1 torr 20 mm). Sample weight: 53.6 mg

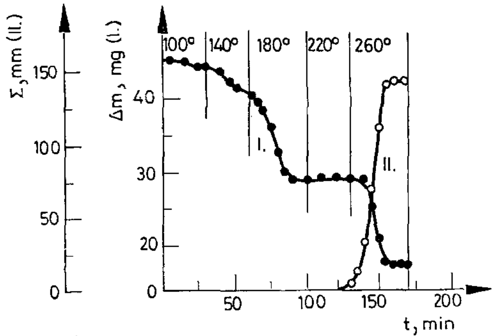

Fig. 3. Weight losses of $Cu(ClO_4)_2 \cdot 6\,H_2O$ at different temperatures. At a given temperature the sample was treated to $\Delta w = 0$. Sample weight: 45 mg

The weight loss of 3.79% at 100° can in all probability be ascribed to the desorption of adsorbed water. The weight loss of 10.18% at 140°, referred to the weight remaining after treatment at 140°, corresponds to the splitting-off of 2 molecules of crystal water. The loss at 180°, 25.24%, is higher than the value, 21.52%, corresponding to complete dehydration. No change in weight occurred at 220°. The copper(II) perchlorate decomposed irreversibly at 260°. The weight loss measured in vacuum on the decomposition of the compound is less than the value calculated from equation (1). Copper(II) chloride in small quantity was also found in the solid residue.

Kinetic measurements

The thermal decomposition of copper(II) perchlorate was studied under isothermal conditions in the range 240–270°, by simultaneous measurement of the weight loss of the sample and the pressure of oxygen evolved. The sample was pretreated at 150° for 30 min. Some α *vs.* t curves are shown in Fig. 4.*

Table 1

Kinetic data on the decompositions of the perchlorates

Temperature, °	$Cu(ClO_4)_2$		$Ni(ClO_4)_2$			$Co(ClO_4)_2$		$Mn(ClO_4)_2$		
	$k \cdot 10^2$		$k \cdot 10^3$							
	pressure meas.	weight meas.	Temp.°	pressure meas.	weight meas.	Temp. °	$k\tau\ 10^3$	Temp. °	τ min	k_α
245	2.05	1.65	260	1.75	5.94	150.5	6.69	182.5	884	0.0127
250	2.15	2.25	265	2.67	6.29	156	9.35	185.5	288	0.0160
255	3.20	3.95	271	3.92	7.80	160	12.4	190	147	0.0160
260	4.45	4.50	280	9.70	11.60	165.5	18.4	195	69	0.0243
265	5.30	5.65	290	22.94	24.3	171.5	24.0	200	30	0.0285
Activation energy (kcal/mole)	43.7	45.9		49.0	52.0		24.8		64.0	21.4

The k values were calculated from the Avrami-Erofeyev equation, $[-\log(1-\alpha)]^{1/n} = kt + C$; $(n = 3)$].

τ: time lag

k_α slope of linear segments of the α *vs.* t curves

The reaction begins immediately after the time necessary for heating-up of the sample, without an induction period. The weight and pressure measurements gave practically the same decomposition curve. Mathematical evaluation of the α *vs.* t curves was performed with the Avrami–Erofeyev equation. This proved valid for $\alpha = 0.1-0.8$. The activation energy turned out to be 43.7 (pressure measurement) and 45.9 (weight measurement) kcal/mole.

The kinetic data are listed in Table 1.

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* α = fraction of the perchlorate decomposed. In the pressure measurements: $\alpha = \frac{p_t}{p_f}$, where p_t = the pressure of gases at time, t, and p_f = final pressure. In the weight-loss measurements: $\alpha = \frac{w_K - w_0}{w_K}$, where w = weight of the sample, w_K = weight of the decomposed material, w_f = weight of the solid residue, w_t = weight measured at time t, $w_0 = w_t - w_f$ and $w_K = w - w_f$.

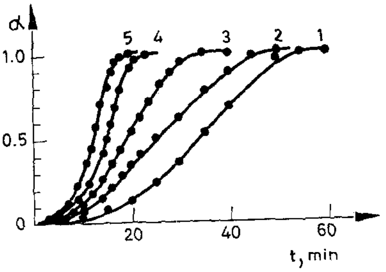

Fig. 4. α *vs.* t curves for the isothermal decomposition of $Cu(ClO_4)_2$: 1. 245°, 2. 250°, 3. 255,° 4. 260°, 5. 265°. Sample weight: 100 mg

Nickel(II) perchlorate

Thermoanalytical studies

According to the termoanalytical curves of $Ni(ClO_4)_2 \cdot 6H_2O$, weight loss in air begins at 50°. The initial slow loss continues up to 280−290°. This weight decrease amounts to 18%, which corresponds to the splitting-off of approximately 4 molecules of water. Two endothermic peaks are found in this temperature range, at 112 and 235°. Fast decomposition began above 290°, and was complete at 370°.. The two peaks at 310 and 352° in the DTG and DTA curves show that two different processes take place during the decomposition. The end-product consisted of NiO containing a slight oxygen excess (active oxygen). The overall weight loss was 79.5%, which corresponds to the reaction

$$Ni(ClO_4)_2 \cdot 6H_2O = NiO + Cl_2 + 3.5O_2 + 6H_2O \qquad (2)$$

The theoretical loss for this reaction is 79.57%.

Figure 5 shows a termoanalytical curve taken in vacuum at a heating rate of 2.5°/min. The sample decreases in weight up to 260° without break. The

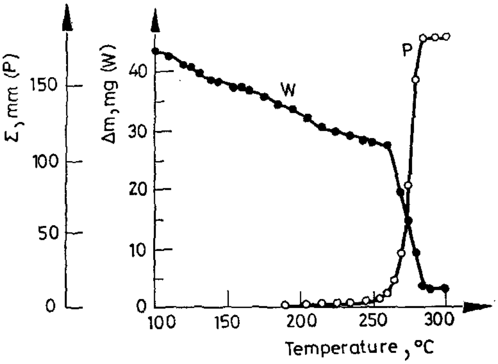

Fig. 5. Decomposition of $Ni(ClO_4)_2 \cdot 6\,H_2O$ in vacuum. Heating rate: 2.5°/min. *W*: weight loss, *P*: pressure of oxygen evolved. Sample weight: 46.2 mg

weight loss is 39.1%, which is substantially more than the value of 29.5% for complete dehydration. Up to 250°, evolution of oxygen is extremely slight. Rapid decomposition, together with commencement of oxygen evolution, occurs above 260°. The weight loss is completed at 290°.

The fact that the weight loss measured prior to the beginning of oxygen evolution was considerably in excess of the value for complete dehydration, indicates that the dehydration is accompanied by the parallel splitting-off of perchloric acid:

$$Ni(ClO_4)_2 \cdot 6H_2O = Ni(OH)ClO_4 + HClO_4 + 5H_2O \qquad (3)$$

The overall reaction was associated with a weight loss of 47.9%. The formation of perchloric acid was detected by chemical analysis at as low as 160°. When the solid sample was maintained at consecutively higher temperatures in vacuum, until weight constancy, a weight loss of 23.2% was obtained at 160°, and one of 14.6% at 200°. Decomposition accompanied by oxygen evolution was first observed at 260°.

When the material was pretreated to weight constancy, and the experiments were then continued at 265°, first a rapid decomposition without oxygen evolution was obtained, and then a slow decomposition with considerable oxygen evolution. The latter decomposition step was preceded by an inductionp eriod of a few minutes. The total weight loss on pretreatment and in the first stage at higher temperature was 47–49%. This points to the occurrence of reaction (3).

Kinetic measurements

Kinetic measurements were made at 260–300° on material pretreated at 150°. In this case too the decomposition of the compound was followed by simultaneous measurement of the weight decrease and oxygen evolution. Figure 6 presents α *vs.* t curves for the decomposition accompanied by oxygen evolution.

The decomposition is of an autocatalytic nature. Mathematical description of the decomposition curves was attempted with the Prout–Tompkins and the Avrami–Erofeyev equations. The latter proved more suitable, describing the decomposition for α = 0.1–0.8. From the temperature-dependence of the rate

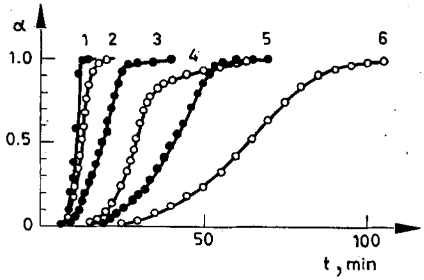

Fig. 6. α *vs.* t curves for the isothermal decomposition of $Ni(ClO_4)_2$: 1. 274°, 2. 270°, 3. 265°, 4. 261°, 5. 256°, 6. 250°. Sample weight: 100 mg

constants an activation energy of 52 kcal/mole was obtained from the weight measurements, compared with 49.0 kcal/mole from the pressure measurements. On preliminary addition of the solid reaction product the reaction began sooner and was completed more quickly. The rate maximum was shifted towards the initial stage of the decomposition. A similar catalytic effect was also exerted by pure nickel(II) oxide.

Cobalt(II) perchlorate

Thermoanalytical studies

Thermal measurements indicated that the partially dehydrated material, $Co(ClO_4)_2 \cdot 3H_2O$ undergoes decomposition in air in three steps, at 80–183, 183–253 and 253–290°. The weight losses for these temperature ranges are 6.06%, 18.18% and 54.5%. All three decomposition steps are accompanied by endothermic heat changes.

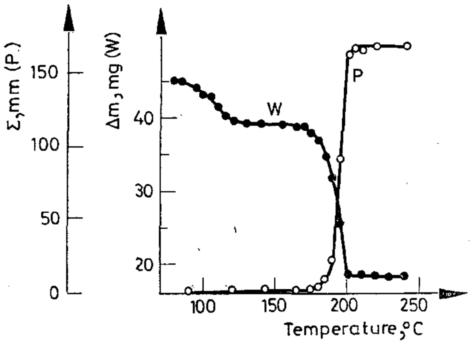

Fig. 7. Decomposition of $Co(ClO_4)_2 \cdot 3\,H_2O$ in vacuum. Heating rate: 2.5°/min. *W*: weight loss, *P*: pressure of oxygen evolved. Sample weight: 45 mg

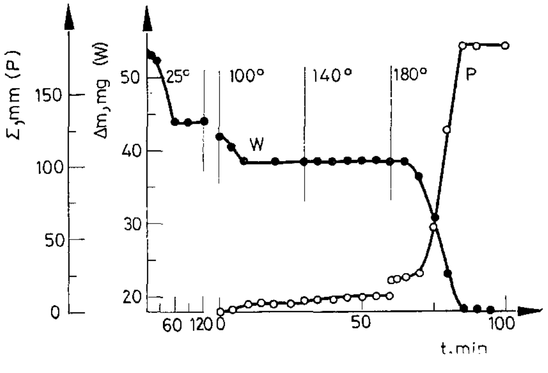

Fig. 8. Weight losses of $Co(ClO_4)_2 \cdot 3\,H_2O$ at different temperatures. At a given temperature the sample was treated to $\Delta w = 0$

On the basis of the overall weight change, the decomposition can be described by the following equation:

$$Co(ClO_4)_2 \cdot 3H_2O = 1/3Co_3O_4 + Cl_2 + 10/3O_2 + 3H_2O \qquad (4)$$

The weight decrease measured in vacuum with a heating rate of 2.5°/min prior to the gas evolution indicative of the irreversible decomposition (180°), 24.2%, exceeds the value corresponding to the loss of the three molecules of crystal water (18.18%) (Fig. 7). Here again, this shows that perchloric acid too is lost in parallel with the dehydration, before commencement of the irreversible decomposition.

The results of thermogravimetric measurements made to weight constancy at the individual temperatures are to be seen in Fig. 8. Based on the measured weight losses, it is concluded that water loss proceeds already at 100°. The percentage weight loss, however, 25.2%, is again larger than the theoretical value. The weight of the sample remained constant at 140°. Irreversible decomposition of the compound began at 180° and continued up to 205°. The weight loss confirms the above decomposition equation.

Kinetic measurements

Kinetic examinations were carried out between 150 and 200° with material pretreated in vacuum for 30 min at 110°. The α *vs.* t curves recorded from the weight and pressure measurements are of an autocatalytic nature. Some α *vs.* t curves are shown in Fig. 9. The Avrami–Erofeyev equation proved to hold in the range $\alpha = 0.1-0.90$. The activation energy was 24.8 kcal/mole.

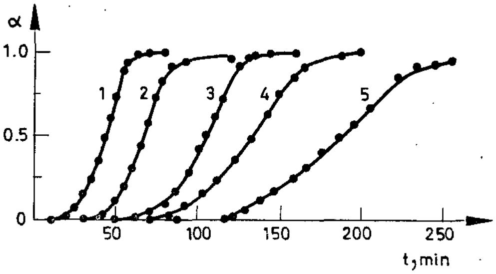

Fig. 9. α *vs.* t curves for the isothermal decomposition of $Co(ClO_4)_2$: 1. 171.5°, 2. 165°, 3. 160°, 4. 156°, 5. 150.5°. Sample weight: 100 mg

Manganese(II) perchlorate

Thermoanalytical studies

The first decomposition step in the derivatogram of $Mn(ClO_4)_2 \cdot 6H_2O$ (Fig. 10) appeared between 107 and 248°; this was associated with a broad endothermic peak at 146° in the DTA curve. The weight loss of 21.5% approximates to the value calculated for the splitting-off of 4 molecules of crystal water, 19.9%.

Rapid decomposition of the compound begins at 248°, the process being accompanied by an endothermic heat change. The overall weight decrease measured for the two stages was 78.5%. Chemical analysis indicated that the solid residue consisted of a mixture of MnO_2 and Mn_2O_3. The calculated weight loss for MnO_2 formation is 75.98%, and for Mn_2O_3 formation is 78.19%.

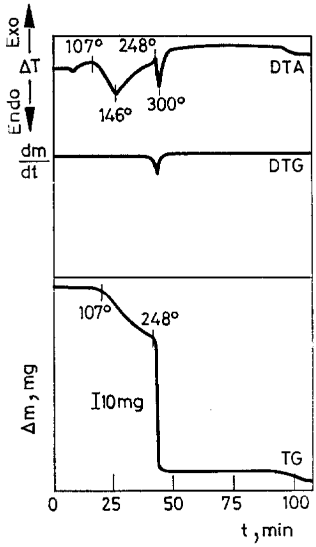

Fig. 10. DTG, DTA and TG curves for the thermal decomposition of $Mn(ClO_4)_2 \cdot 6\,H_2O$ in air. Heating rate: 6°/min. Sample weight: 200 mg

At a heating rate of 2.5°/min in vacuum, the compound undergoes a weight loss of 22.3% in the range 110–190°. Oxygen evolution and the irreversible decomposition of the compound begins at 205°, and is complete at 240°.

Kinetic studies

Material pretreated in vacuum for 30 min at 150° was used for the kinetic studies. The experiments were carried out at 180–210°. Identical α *vs.* t curves were obtained from the pressure and weight measurements; some of these are presented in Fig. 11. Decomposition proceeds in 4 stages: (a) a brief stage without decomposition; (b) an acceleratory period, $\alpha = 0.0-0.23$; (c) a stage of constant rate, $\alpha = 0.23-0.76$; (d) a short breakdown stage.

Decomposition occurs predominantly in the constant-rate stage. From the temperature-dependence of the time (τ) of the set of the fast decomposition, obtained on extending the linear sections of the decomposition curves, an activation energy of 64 kcal/mole was calculated. In contrast, the temperature-depend-

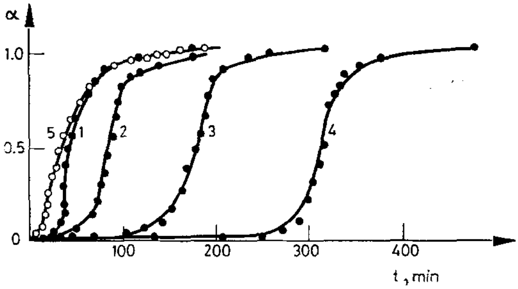

Fig. 11. α *vs.* *t* curves for the isothermal decomposition of $Mn(ClO_4)_2$: 1. 200°, 2. 195°, 3. 190°, 4. 185°, 5. the effect of 10 wt% decomposition residue at 185°. Sample weight: 100 mg

ence of the slopes of the linear sections resulted in an activation energy of only 21.4 kcal/mole.

Preliminary addition of solid decomposition residue to the manganese(II) perchlorate led to the exertion of an extremely large catalytic effect (Fig. 11). At 185° the value of τ was lowered from 288 to 8 min.

Kinetic data on the decompositions of the compounds are given in Table 1.

Discussion

Account were given earlier of the thermal decompositions of chromium(III) perchlorate [15] and iron(III) perchlorate [16]. Taking into account the results reported there, it may be stated in general that the perchlorates of the transition metals are substantially less stable compounds than the alkali metal [1] or alkaline earth metal perchlorates [2]. Anhydrous compounds can not be prepared by thermal treatment; dehydration is accompanied by parallel loss of perchloric acid, with formation of the basic salt:

$$M(ClO_4)_2 \cdot xH_2O = M(OH)ClO_4 \,.\, (x-1)H_2O + HClO_4$$

After the reporting of our experimental results [13] and their utilization in the study of the catalytic decomposition of perchloric acid [8–11], a paper appeared by Vilcu and Georgescu [12] on a kinetic study of the thermal decompositions of transition metal (Mn, Fe, Co, Ni and Cu) perchlorates. From several respects there are essential differences between their data and our experimental results. In some cases they found the temperature range for decomposition of a given transition metal perchlorate to be 100–150° lower than we found. In their experiments the crystalline perchlorates (with the exception of copper perchlorate) were dried in vacuum for 3–4 hours at 100–115°, and then for 4 hours at 150°. Directly before the thermogravimetric examinations the samples were treated further for 30 min in argon at 110°. The decompositions of the compounds were studied in vacuum, at the following temperatures: manganese(II) perchlorate:

125 – 155°; iron(II) perchlorate: 90 – 135°; cobalt(II) perchlorate: 150 – 185°; nickel(II) perchlorate: 130 – 170°: copper(II) perchlorate: 80 – 110°. The progress of the decomposition was followed by measurement of the weight decrease.

They claimed that these perchlorates decompose to oxide and chloride at high rate even below 200°. Data on the extents of the weight decreases were not given, merely α *vs. t* curves being reported. Depending on the temperature, these attain saturation values in the range $\alpha = 0.3 - 0.8$; although the method given for calculation of the α values is not completely unambiguous, this permits the conclusion that in the temperature range under consideration the extent of the weight change (decomposition ?) varies with the temperature. This casts great doubt on the kinetic evaluation of the measurements. A further problem is that the perchlorates were at times subjected to preliminary heat-treatment at a temperature 30 – 50° higher than the temperature range of the kinetic measurements.

Our measurements show that there is indeed a weight decrease below 200°, but that this can be ascribed to loss of the water and some of the perchloric acid. Oxygen evolution indicative of irreversible decomposition occurs at a much higher temperature. For the sake of completeness, we too carried out a number of experiments in the manner described by the above authors [12]. Subsequent to the pretreatments, oxygen evolution was not observed in a single case even at the low temperature indicated. Accordingly, it appears probable that the weight decreases measured in that work [12] can not, or to only a slight extent, be attributed to the irreversible decompositions of these perchlorates.

Mechanism of the decomposition

In the decomposition we have to consider the following steps [1,2]:

$$ClO_4^- \rightleftharpoons ClO_3^- + O \quad (5)$$

$$ClO_3^- \rightleftharpoons ClO_2^- + O \quad (6)$$

$$ClO_3^- \rightleftharpoons \tfrac{3}{4}\,ClO_4^- + \tfrac{1}{4}\,Cl^- \quad (7)$$

$$ClO_2^- \rightleftharpoons ClO^- + O \quad (8)$$

$$ClO_2^- \rightleftharpoons \tfrac{2}{3}\,ClO_3^- + \tfrac{1}{3}\,Cl^- \quad (9)$$

$$ClO^- \rightleftharpoons Cl^- + O^{2-} + O \quad (10)$$

In the case of formation of oxides the last step possibly involes the bimolecular decomposition of ClO^- [17]

$$2\,ClO^- \longrightarrow Cl_2 + O^{2-} + O \quad (11)$$

Our kinetic studies in connection with the thermal decompositions of the various chlorites [18], chlorates [19] and perchlorates [1, 2, 20] quite clearly show that the slow, rate-determining step in the decompositions of metal perchlorates is the first reaction: the splitting of the Cl–O bond. In all cases the other steps involve substantially faster processes. Stepwise decomposition of the perchlorates is supported by the fact that in several cases it proved possible to identify the chlorate ion formed transitionally during the decomposition.

Although chlorate was not found as an intermediate in a single case in the present work, in our view it is probable that the transition metal perchlorates also decompose in a stepwise manner, and that the slow, rate-determining process here too is the splitting of the Cl–O bond. The activation energies for decomposition of the alkali metal, the alkaline earth metal and silver perchlorates were in good agreement with the endothermic reaction heat of the above process (assuming atomic oxygen formation) and with the dissociation energy of the Cl–O bond, 64.292 kcal/mole [21]. In the present case the activation energy values are substantially smaller than the dissociation energy of the Cl–O bond, particularly in the cases of chromium and cobalt perchlorates.

A part is probably played in the development of the lower activation energy by the high polarizing powers of the transition metal ions. In addition, the decrease of the activation energy may be induced too by the fact that oxides are formed on the decompositions of the transition metal perchlorates, and that these may exert a significant catalytic effect. The latter assumption is strengthened by the circumstance that the oxides of the transition metals accelerate the decompositions of the alkali metal perchlorates and chlorates. In their presence the decompositions proceed at temperatures lower by 100–150°, and with substantially lower activation energies. The fact that prior addition of the oxides to the transition metal perchlorates exerted a relatively slight effect on the course of the reactions can be explained in that the oxide nuclei developed already during the dehydration process preceding decomposition of the perchlorate ion, i.e. in the course of formation of the basic salt.

An exception is the thermal decomposition of manganese perchlorate, where the solid decomposition product ($MnO_2 + Mn_2O_3$) exerted an extremely large catalytic effect. It may be mentioned that the lowest degree of perchloric acid formation prior to the commencement of oxygen evolution indicating perchlorate ion decomposition was observed in this case. It is highly probable that the non-catalyzed reaction proceeds in the slow process preceding the fast decomposition, while MnO_2-catalyzed decomposition takes place in the fast stage. The activation energy values are in accord with this explanation; the activation energy calculated for the initial slow reaction, 64 kcal/mole, agrees well with the dissociation energy of the Cl–O bond. The activation energy found for the fast process is much lower than this.

In some cases, decomposition of the transition metal perchlorates was accompanied by oxidation of the metal ion (chromium, cobalt, manganese), and an appreciable proportion of the solid end-product consisted of the oxide of a higher-valency metal ion. The lowest activation energies were obtained in these cases. As already concluded in the discussion of the thermal decomposition of chromium perchlorate [15], it is conceivable that in such a case the stepwise decomposition of the perchlorate ion plays a minor role, and formation of the higher-valency metal ion oxide is a consequence of rearrangement within the molecule, and internal oxidation.

Factors determining the stabilities of the compounds

It was earlier stated that the thermal stabilities of the alkali metal and alkaline earth metal chlorates and perchlorates are determined by the ionic character of the bond between the metal ion and the anion, and by the polarizing power (effective electric field strength) of the metal ion [1, 2, 18, 19]. The larger the effective electric field strength, F^*, of the metal ion, and the smaller the percentage ionic character of the compound, the lower the stability of the compound. In our view, these factors also play a role in determining the thermal stabilities of the transition metal perchlorates. Since the decompositions of the compounds are described by various kinetic equations, it seemed to be more appropriate to characterize the stabilities of the compounds not by a comparison of the rate constants, but via the temperature at which oxygen evolution begins (T_0) or that at which 50% of the oxygen has been evolved (T_{50}), the heating rate being 2.5°/min. Data on these temperatures and the relevant metal ions are given in Table 2.

From the tabulated data it can be established that the chromium(III) ion has the greatest effective field strength, and accordingly forms the most unstable perchlorate as regards the ions considered. With the decrease of F^*, the stabilities of the perchlorates increased in the sequence Cr < Fe < Cu < Ni. However,

Table 2

Some characteristic features of the transition metal ions and data for the thermal stabilities of perchlorate salts

Ion	r	z^*	F^*	T_{50}
Cr^{3+}	0.64	3.752	9.173	165
Cr^{4+}	0.60	5.086	14.127	
Fe^{3+}	0.67	3.6672	8.167	245
Cu^{2+}	0.72	3.4333	6.627	268
Ni^{2+}	0.78	3.1047	5.106	275
Co^{2+}	0.82	3.0188	4.492	198
Co^{3+}	0.64	3.9372	9.612	
Mn^{2+}	0.91	2.6672	3.221	230
Mn^{3+}	0.70	3.9791	8.12	
Mn^{4+}	0.52	4.7520	17.60	

r: radius of the metal ion (Goldschmidt)
z^*: effective charge of the metal ion [22]
$F^* = \frac{z^*}{r^2}$; F^*: effective electric field strength
T_{50}: the temperature of 50% decomposition of the perchlorate salts at a heating rate of 2.5°/min.

cobalt and manganese perchlorates proved to be essentially more unstable compounds than would have been expected on the basis of the effective electric field strengths of the cobalt(II) and manganese(II) ions. The cause of the different behaviour of cobalt and manganese perchlorates is in our opinion that the metal ions undergo oxidation when the compounds decompose. This means that the polarizing powers of the higher-valency metal ions formed during the oxidation must also be taken into account in the assessment of the effects of the cations. Table 2 gives the effective electric field strengths of Cr^{4+}, Co^{3+}, Mn^{3+} and Mn^{4+}.

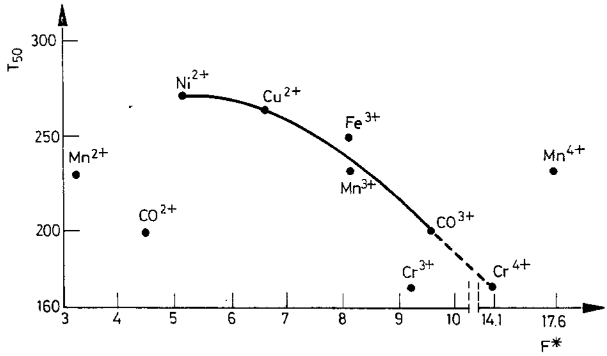

Fig. 12. The thermal stabilities of the perchlorates (T_{50}) and the effective electric field strengths of the cations (F^*). T_{50}: the temperature of 50% decomposition of the perchlorate salts at a heating rate of 2.5°/min

For the sake of clearness, the temperatures characteristic of the stabilities of the perchlorates are plotted in Fig. 12 as a function of the effective electric field strengths of the cations. In those cases where the metal ion was oxidized, the effective electric field strengths of both the lower and the higher-valency metal ions have been taken into consideration.

Although direct proportionality between the F^* and T_{50} values can not be established in this case either, the effective electric field strengths of the cations have a clear role in determining the stabilities of the compounds.

If the stabilities of the metal perchlorates are compared with the effects of the corresponding oxides on the vapour-phase decomposition of perchloric acid [9], it is seen that the oxides are the more effective, the more unstable the perchlorate salts formed from them. In agreement with the above, an outstandingly high catalytic effect was exhibited by Cr_2O_3. The correlation found confirms the conclusion that the decomposition of perchloric acid proceeds via formation and decomposition of surface perchlorate ion.

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RÉSUMÉ — La décomposition thermique des perchloartes de nickel(II), de cuivre(II), cobalt(II) et de manganèse(II) a été étudiée par analyse thermique et mesures cinétiques. Les perchlorates anhydres n'ont pas pu être préparés par chauffage et traitement sous vide de échantillons; les oxydes ont été obtenus comme produits solides principaux de décomposition. Dans le cas des perchlorates de cobalt et de manganèse, l'oxydation des ions métalliques a été observée pendant la décomposition. Dans la plupart des cas, la décomposition des perchlorates a suivi la cinétique d'Avrami-Erofeyev. Une corrélation a été trouvée entre la stabilité des perchlorates et les intensités effectives des champs des cations.

ZUSAMMENFASSUNG — Die thermische Zersetzung von Nickel(II), Kupfer(II)--, Kobalt(II)- und Mangan(II)-perchloraten wurde mittels Thermoanalyse und kinetischer Messungen untersucht. Durch Erhitzen und Entgasen der Proben im Vakuum konnten keine wasserfreien Perchlorate hergestellt werden; Oxide wurden als feste Hauptzersetzungsprodukte erhalten. Im Falle der Perchlorate von Kobalt und Mangan wurde die Oxidation der Metallionen während der Zersetzung beobachtet. In den meisten Fällen verlief die Zersetzung der Perchlorate nach der Kinetik von Avrami-Erofeyev. Eine Korrelation wurde zwischen den Stabilitäten der Perchlorate und der tatsächlichen Feldstärke der Kationen gefunden.

Резюме — С помощью термического анализа и кинетических измерений изучено термическое разложение перхлоратов двухвалентных никеля, меди, кобальта и марганца. Безводные перхлораты не могут быть получены нагреванием и обезгаживанием образцов в вакууме; в качестве основных твердых продуктов разложения были получены окиси. В случае перхлоратов кобальта и марганца, во время разложения наблюдалось окисление ионов металла. В большинстве случаев разложение перхлоратов подчиняется кинетике Аврами-Ерофеева. Установлена корреляция между стабильностью перхлоратов и силой эффективного поля катионов.