KINETICS AND MECHANISM OF THE THERMAL DECOMPOSITION OF METAL CHLORITES, CHLORATES, AND PERCHLORATES

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Studies related to the thermal decomposition of different metal chlorites, chlorates and perchlorates are reviewed and a critical survey on various interpretations of the thermal behaviour of these salts is given.

Introduction

Halogen oxyacids and their salts occupy an important place in the system of inorganic chemistry. During the past twenty years there has been particularly great interest in this family of compounds, as demonstrated by the several hundred publications on their physical and chemical properties, and primarily on their thermal stabilities. The main cause of this great interest is that many of these compounds are widely used in practice as source of oxygen. They comprise one of the most important constituents of solid propellants, and are also employed in various pyrotechnic and explosive mixtures.

The primary aims of the present work are to review the considerable experimental and theoretical material, to emphasize on the more important results, and to discuss these at a high level.

Thermal stability of alkali chlorites

According to early observations, sodium chlorite is easily explosible on shock; when heated, chlorate and chloride is formed, accompanied by a slight amount of oxygen evolution (see [1, 2]). TAYLOR *et al.* [3] stated that sodium chlorite is highly resistant to long period of storing at room temperature: after 10 years of storage its weight loss was negligible and, as can be seen from Table I, its composition has not much altered either.

At higher temperatures (150° C) decomposition was not observed after 30 minutes, above 200° C, however, a considerable amount of chlorate formation was noted. It has also been observed that sodium chlorite explode only if the surface of the metal performing the striking contained grease.

The thermal stability of chlorites has been studied in detail only recently applying derivatographic methods as well as kinetic measurements [1].

Table I

The composition of solid NaClO$_2$ *after different storing
periods at 25° C* [3]

Compound	Composition in weight %			
	Starting material	after 4 months	after 22 months	after 130 months
NaClO$_2$	84.90	87.00	87.59	86.63
NaCl	2.40	2.28	2.05	2.77
NaClO	0.00	0.00	0.11	0.00
NaClO$_3$	2.96	1.76	1.35	1.97
Na$_2$CO$_3$	13.52	10.12	7.47	9.17
	103.78	101.16	98.57	100.54

The derivatograms of sodium chlorite are plotted in Fig. 1.*a*. There are three exothermic peaks on the DTA curve, at 191, 273° and 557° C. An endothermic change appeared at 260° C. From the first two exothermic peaks only the second was connected with a very slight but reproducible weight loss (about 1%). The decomposition of the substance started at 440—450° C. On increasing the heating rate (from 3° C/min. to 18° C/min.) the exothermic peaks and also the onset of the loss of weight were shifted towards higher temperature.

Interrupting the measurements after the second exothermic process at 280° and 320° C and cooling down the sample, the substance did not exhibit in a repeated experiment the exothermic peaks previously observed (Fig. 1.*b*).
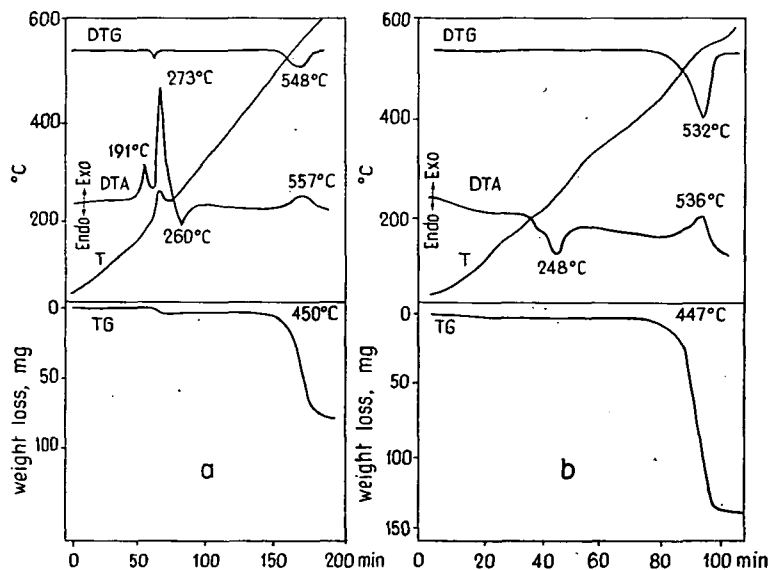

Fig. 1. Derivatogram of NaClO$_2$ (a). Derivatogram after the interruption at 280° C (b). Weight of substance: 210 mg; heating rate: 6° C/min. [1]

The solid residue obtained at the interruption did not contain any sodium chlorite: its composition was: 73.7% $NaClO_3$ and 24.3% $NaCl$. These results show that under the experimental conditions applied sodium chlorite is transformed into sodium chlorate and sodium chloride according to the equation

$$3\,NaClO_3 = 2\,NaClO_3 + NaCl. \tag{1}$$

The exothermic character of the reaction is in accordance with the reaction heat calculated from the heats of formation of the substances (Table II). The endo-

Table II

Heat of reaction of different transformations of chlorites

Compound	Heat of formation kcal/mole	ΔH_1/mole	ΔH_2/mole	ΔH_3/mole	ΔH_4/mole
$LiClO_2$	−84.88	+13.98	+5.01	−12.82	+27.36
$NaClO_2$	−72.65	−13.08	−17.24	−25.58	+45.90
$KClO_2$	−78.90	−14.60	−18.15	−25.27	+71.40
$RbClO_2$	−74.50	−17.50	−21.13	−28.41	+70.1
$CsClO_2$	−74.46	−19.54	−22.04	−29.04	+73.02
$Ba(ClO_2)_2$	−158.2	−23.5	−31.45	−47.36	+25.2
$AgClO_2$	0.0	−5.73	−13.9	−30.36	+3.26
$Pb(ClO_2)_2$	—	—	—	—	—

ΔH_1: for $MeClO_2 + \dfrac{1}{2} O_2 = MeClO_3$

ΔH_2: for $MeClO_2 = \dfrac{2}{3} MeClO_3 + \dfrac{1}{3} MeCl$

ΔH_3: for $MeClO_2 = MeCl + O_2$

ΔH_4: for $2\,MeClO_2 = Me_2O + Cl_2 + \dfrac{1}{2} O_2$

thermic change experienced at 260° C as well as the decomposition which started above 448° C were due to melting and decomposition of the sodium chlorate. The latter process is characterized on the DTA curves by an exothermic peak. If the interruption was carried out at 160° C, *i.e.* before the appearance of the first exothermic peak, only 5% $NaClO_3$ was found in the sample.

The derivatogram of sodium chlorite was taken in the presence of sodium chlorate and sodium chloride, respectively (mole ratio 1:1). It appeared that the products of the disproportionation reaction did not essentially influence the characteristics of sodium chlorite transformation.

The derivatographic study of the other alkali metal chlorites is hampered to a considerable extent by the fact that these compounds are appreciably more hygroscopic than sodium chlorite. Their thermal behaviour is similar to that of sodium chlorite [2]. The sharp exotherm peak indicating the disproportionation reaction is accompanied by only an extremely small weight loss (1—2%) on the TG curve (Fig. 2).

The data concerning the thermal transformation of the compounds are listed in Table III.

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Table III

Exothermic peaks on DTA curves belonging to the disproportionation of chlorites [1, 2, 4]

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Compound	$LiClO_2$	$NaClO_2$	$KClO_2$	$RbClO_2$	$CsClO_2$	$Ba(ClO_2)_2$	$Pb(ClO_2)_2$	$AgClO_2$
°C	210	191	185	155	120	220	123.5	95

Comparison of the thermal behaviour of the alkali metal chlorites shows that the beginning of the exothermic peak belonging to the disproportionation of the chlorites

$$MClO_2 = \frac{2}{3} MClO_3 + \frac{1}{3} MCl \qquad (2)$$

decreases from lithium to cesium. On the other hand, the temperature of the weight decrease corresponding to the decomposition of the chlorate at higher temperature increases from lithium to cesium.

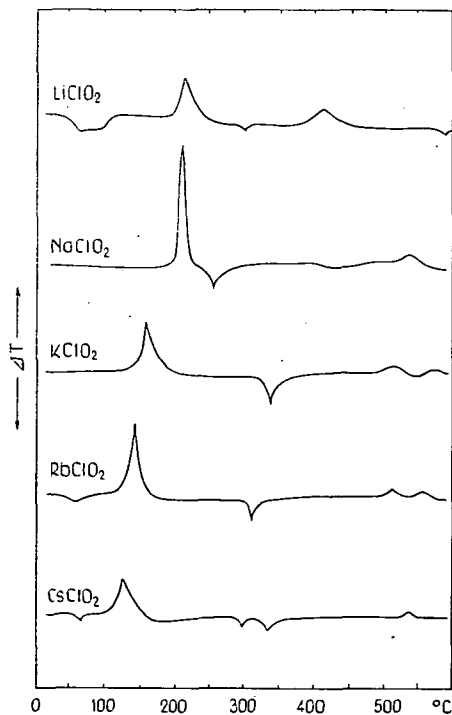The kinetics of the disproportionation of alkali chlorites, under isothermal condition, has been studied in the temperature range between 52 to 180° C. [1, 2]. The reaction starts without induction period and its rate increases with increasing temperature. The reaction is adequately described by the first order equation up to 50—70% and 30—40% conversion at higher and lower temperatures, respectively.

The temperature of the disproportionation reaction decreased from lithium (152—180° C) to cesium (52—98° C). The activation energies were found to vary between 15—28 kcal/mole. Many attempts have been made to decompose sodium chlorite under isothermal conditions. However, the substance only disproportionated into chlorate and chloride even at higher temperatures, (300—400° C) without any gas evolution. The slow gas evolution experienced above 400° C is the result of the decomposition of sodium chlorate formed in the disproportionation. The same behaviour was found for the other alkali chlorites.

Fig. 2. DTA curves of alkali chlorites in air. Heating rate 3°/min. [2]. Weight of substance: 50 mg

Thermal stability of barium, silver and lead. chlorites

Among the other metal chlorites, detailed studies were carried out only on barium, lead and silver chlorites [1, 4].

The thermal behaviour, the TG and DTA curves of these compounds essentially differred from that of the alkali chlorites. Parallel to the large heat evolution, extremely fast decomposition appeared on the TG curve at the following temperatures (Figs. 3 and 4):

barium chlorite 190° C,
silver chlorite 120° C,
lead chlorite   103° C.

On applying 1°/min heating rate, the behaviour of chlorites altered, namely they were converted almost at the above temperatures into chlorates and chloride accompanied by an exothermic heat change without any decomposition.

The direction of conversion of barium chlorite was influenced by addition of foreign substances (barium chloride, barium chlorate, aluminium oxide, nickel oxide.) In such cases, decomposition of the compound did not occur even when 6°/min. heating rate was used. All these findings indicate that the direction of conversion of barium, silver, and lead chlorite — contrary to that of the sodium chlorite — is extremely sensitive to the temperature and to experimental conditions.
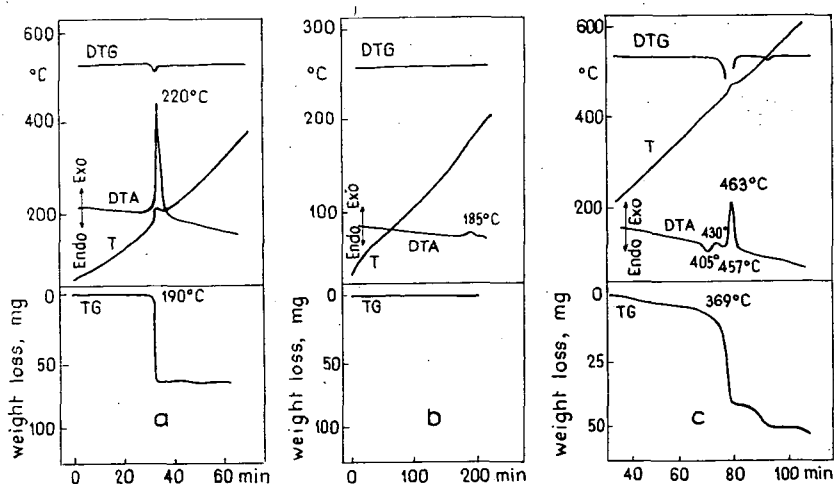

Fig. 3. Derivatogram of $Ba(ClO_2)_2$ [1]. Weight of substance: 160 mg; heating rate: (a) 6°/min.; (b) 1°/min.; (c) continuation of the former measurement with 6°/min.

The disproportionation of barium, lead and silver chlorites has been studied kinetically at lower temperatures, and the activation energies were found to be 23, 26 and 39 kcal/mole. The slow decomposition of barium and lead chlorites could not be studied either, as at the moment of beginning of gas evolution the decomposition

immediately turned into explosion. The activation energies calculated from the temperature dependence of the induction period before the explosion were found to be 38.8; and 28 kcal/mole (Fig. 5). The explosion proved to be of thermal origin; at the moment of explosion the temperature rise was between 40 and 80° C.
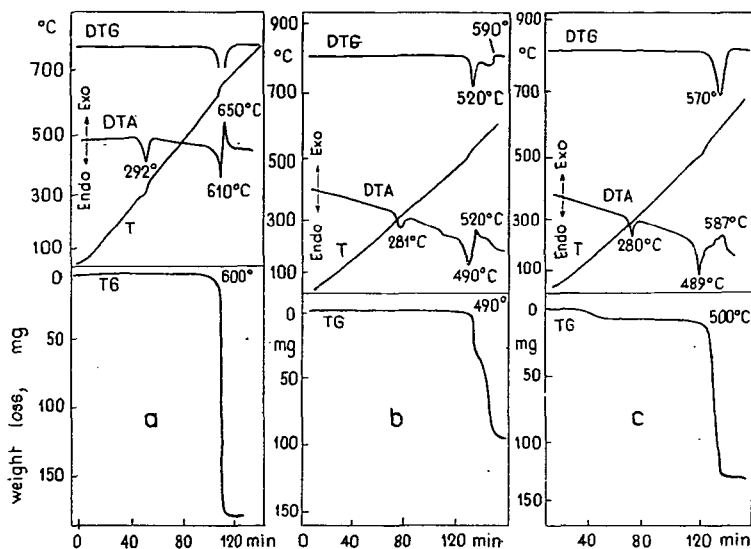
Fig. 4. Derivatogram of $Pb(ClO_3)_2$ [1]. Weight of substance: 100 mg; heating rate: (a) 6°/min.; (b) 1°/min.; (c) continuation at a heating rate of 6°/min. of the measurement interrupted at 150° C
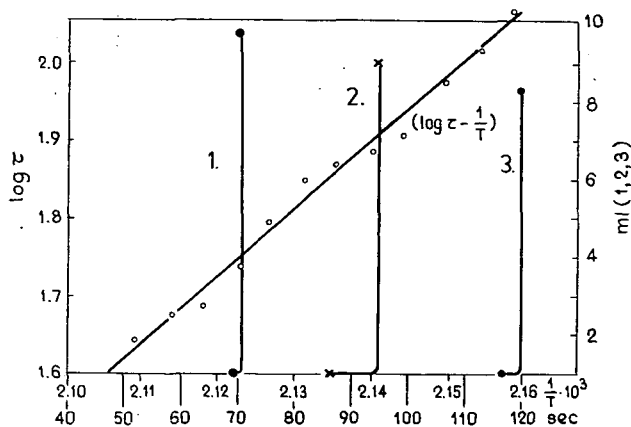
Fig. 5. Explosion of $Ba(ClO_3)_2$ at different temperatures and the Arrhenius diagram of the induction periods [1]; τ = induction period before the explosion, ml = the amount of gases formed during the explosion. (1), at 196° C; (2), at 192° C; (3), at 190° C

Among the chlorites investigated, silver chlorite was the only compound the slow decomposition of which was observed. In vacuum the reaction occurred according to equation

$$AgClO_2 = Ag + ClO_2. \tag{3}$$

The decomposition was of autocatalytic character; the accerelation period followed the equation

$$\log p = k \cdot t + c.$$

The activation energy was found to be 48.2 kcal/mole. In the period following the rate maximum the monomolecular decay equation described the decomposition. The activation energy was 24.8 kcal/mole.

Table IV

Kinetic data for the reactions of chlorites

Compound	Temperature range °C	Methods	Activation energy kcal/mole	Frequency factor min^{-1}	Kinetic equation
Disproportionation					
LiClO$_2$	152—180	chemical analysis in air	24.2	$6.28 \cdot 10^8$	first order
NaClO$_2$	140—160	chemical analysis in air	54.2	$1.85 \cdot 10^{25}$	first order
KClO$_2$	100—140	chemical analysis in air	28.3	—	first order
RbClO$_2$	90—120	chemical analysis in air	20.0	$2.86 \cdot 10^6$	first order
CsClO$_2$	52—98	chemical analysis in air	15.2	$1.11 \cdot 10^5$	first order
Ba(ClO$_2$)$_2$	130—170	chemical analysis in air	23.5	$3.88 \cdot 10^9$	first order
Pb(ClO$_2$)$_2$	75.5—95	chemical analysis in air	39.4	$1.62 \cdot 10^{21}$	first order
Decomposition					
AgClO$_2$	85—105	chemical analysis in air	26.0	$1.74 \cdot 10^{16}$	first order
Explosion					
AgClO$_2$	108—125	in air ml of gases	53.0	—	induction period
Ba(ClO$_2$)$_2$	190—210	in air ml of gases	38.8	—	induction period
Pb(ClO$_2$)$_2$	112—115	in air ml of gases	28.0	—	induction peroid

Data concerning the thermal behaviour of other metal chlorites are very scarce in literature. Calcium and strontium chlorites decompose upon contact with a hot wire, and they explode upon percussion [5]. Zinc and cadmium chlorites containing two moles of crystal water did not explode upon percussion; in vacuum however, they, changed into basic salt accompanied by loss of water and chlorine evolution [5]. Mercurous chlorite decomposes upon heating and percussion to mercurous chloride. Mercuric chlorite explodes upon percussion while chloride is being formed. In greater quantity, it easily explodes at room temperature immediately after its preparation [6]. The light yellow thallium chlorite becomes brownish in 15—20 min after preparation. It decomposes completely at 30° C after 13—15 hours accompanied by a very slight gas evolution. It explodes violently accompanied by sound at 45° C into chlorine, oxygen and a little chlorine dioxide [7]. Nickel chlorite containing two moles of crystal water explodes at a temperature as low as that of the water bath. Upon percussion it explodes similarly as copper chlorite [8, 9]. Kinetic data for the reactions of chlorites are collected in Table IV. Data concerning the physical properties and bonding of the metal chlorites are given in Table V.

Table V

Some physical constants of chlorites

Compounds	Density	Ionization potential of cations eV	F^*	Refractive index n_D^{22}	K Dieletric constant at 350 Kc/s	Absorption edge Å	Optical activation energy E_0 (eV)	Thermal activation energy E_T (eV)	K_0/K	Ionic character of bond %
$LiClO_2$		5.390	2.915		9.213	2875	4.31			67.4
$NaClO_2$		5.138	2.407	1.547	6.535	2660	4.66	1.70	0.366	68.5
$KClO_2$		4.339	1.661	1.529	4.073	2760	4.49		0.5739	73.0
$RbClO_2$		4.176	1.423		4.687	2925	4.23			73.8
$CsClO_2$		3.833	1.303		7.267	3366	3.68			75.1
$Ba(ClO_2)_2$	3.60	10.00	—	1.645	4.215	2900	4.28	2.75	0.642	44.95
$AgClO_2$	4.30	7.56	3.394	2.1	5.282	4050	3.06	2.55	0.835	35.8
$Pb(ClO_2)_2$	5.10	15.03	3.876	2.1	5.417	4000	3.10	2.52	0.814	16.99

$$F^* = \frac{Z^* \cdot e}{r^2} = \text{effective electric field strength of cation}$$

r = radius of cation

Z^* = effective nuclear charge number, $Z^* \cdot e = (Z - S)e$

Z = nuclear charge, S = screening number

$K_0 = n^2$

* The effective electric field strength of barium cannot be calculated due to the lack of data for the determination of its screening number.

Mechanism of disproportionation and decomposition of chlorites

Although the disproportionation of chlorine oxy salts has been known for a long time, however, detailed measurements were carried out only with the alkali chlorates, but even these not from the kinetic point of view. The possible reason for this is that, besides disproportionation, the decomposition of chlorates also

occurs. To evaluate the mechanism of the disproportionation of chlorites, it is advisable to take into account the different views concerning the disproportionation of chlorates. According to GLASNER and WEIDENFELD [10] the atomic oxygen formed during the decomposition of potassium chlorate reacts with the chloride *i.e.* with the solid product of the chlorate decomposition, yielding potassium perchlorate.
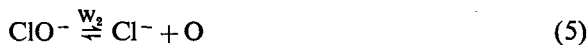
BOSCH and ATEN's [11] isotopic investigations, however, did not prove this conception. According to the calculations of MARKOVITZ, BORYTA and STEWART [12, 13] it is thermodynamically possible that the perchlorate is produced by oxidation of the chlorate with molecular oxygen. However, DODÉ and BASSET's [14] former experiments, in case of sodium chlorate did not give perchlorate even under 1200 atm. oxygen pressure at 475° C. The result was the same when MARKOWITZ kept the mixture of lithium chlorate and lithium chloride under 100 atm. pressure of oxygen at 150° C for several days. Therefore, they described the formation of perchlorate by assuming a reaction between atomic oxygen and chlorate:

$$MClO_3 + O = MClO_4.$$
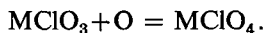
As can be seen in Table II, the oxidation of chlorites by molecular oxygen is thermodynamically also possible. Kinetically, however, it was not observed in any case of chlorites. It may be assumed here, too, that the oxidation proceeds with the assistance of the atomic oxygen formed during the decomposition of chlorite. In this case we should take as the first step the reaction

$$ClO_2^- \overset{W_1}{\rightleftharpoons} ClO^- + O \tag{4}$$

which is followed by the processes

$$ClO^- \overset{W_2}{\rightleftharpoons} Cl^- + O \tag{5}$$

$$ClO_2^- + O \overset{W_3}{\rightleftharpoons} ClO_3^- \tag{6}$$

$$S + O + O \overset{W_4}{\rightleftharpoons} O_2 + M \tag{7}$$

(S = solid surface for the recombination of oxygen atoms.) However the fact that, at a lower temperature, the disproportionation of chlorites occurs without gas formation and, moreover sodium chlorite does not decompose at all, raises some doubt about the internal oxidation mechanism.

The failure of the oxygen atoms to recombine can be accepted only if $W_4 \ll W_3$. Since the rates of both reactions depend on the rate of formation of oxygen atoms, a further condition of the absence of oxygen formation is that

$$W_1 \ll W_3.$$

Although these reaction rate relations cannot be excluded, it would be expected that at high temperature, when W_1 and W_2 have very high values (and thus the oxygen atoms form rapidly), the recombination reaction proceeds with measurable rate, too. In the case of sodium chlorite the oxygen evolution was less than 1% even at 400° C, when the disproportionation reaction occurred instantaneously. If we accept the formation of, and oxidation by, atomic oxygen when sodium chlorite is heated up to an elevated temperature, but still below the disproportio-

6*

nation temperature of sodium chlorate, the oxygen atom should oxidize not only the remaining chlorite, but — to a smaller extent — the formed chlorate, too. From pure sodium chlorite, however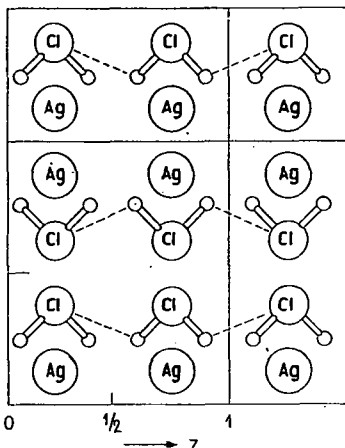, sodium perchlorate did not form even at 200, 300, 350 and 400° C [1]. It is true that below 400° C the transformation of pure sodium chlorate into perchlorate proceeds extremely slowly. However, this cannot be motivated by assuming that at this temperature atomic oxygen (if perchlorate is formed from atomic oxygen) is incapable of oxidizing the chlorate. It is much more reasonable to suppose that at this temperature the chlorine-oxygen bond does not split in sodium chlorate.

On the basis of the above considerations, it seems more acceptable that chlorate formation is the result of a rearrangement taking place inside the lattice without formation of atomic oxygen. This is connected with a release of 13—30 kcal/mole heat of reaction. The transformation of chlorites can be thought to happen by the effect of heat, simultaneously with the vibration and the weakening of the Cl—O bond, an interaction is taking place between the oxygen of chlorites and the chlorine ions of the neighbouring chlorite. This state, owing to the greater thermodynamic stability of chlorate, rearranged to form chlorate and chloride. This process is illustrated in Fig. 6.

Fig. 6. The structure of AgClO₂ viewed along the a axis. The dashed lines indicate the planes of new Cl—O bonds formed during the disproportionation

Whichever mechanism is accepted, the step to be activated in the disproportionation of chlorites obviously is the rupture of the original Cl—O bond. According to the internal oxidation mechanism the activation energy of the reaction should be consistent with the value of the dissociation energy of the chlorine—oxygen bond. The calculated value of the latter is 64.295 kcal/mole [15]. In the decomposition of chlorates and perchlorates, where this step proved to be the rate determining reaction, nearly the same activation energies were obtained (see later). In the present case the activation energies of the reaction were significantly lower. In our opinion the values of activation energy are in better agreement with a rearrangement process taking place between the chlorite ions. In this case, owing to the formation of the new Cl—O bond, evidently a smaller value of energy is needed for the breaking of the original Cl—O linkage. In the most favourable case (if the fractional decomposition $\alpha = 1$) the value of activation energy will be equivalent to the differences between the dissociation energies of the chlorine—oxygen bonds in the two compounds, i.e.

$$E = D_{dissociating} - \beta D_{forming}. \qquad (\beta = \text{constant})$$

As a primary step in the explosion of chlorites, two reactions, the electron transfer process and the rupture of Cl—O bond can be taken into account. In the case of barium chlorite, however the reaction products as well as the activation energy calculated from the temperature dependence of induction periods contradict to this mechanism.

As the explosion of chlorites is preceded by an extremely slight decomposition, it was assumed that the disproportionation of chlorites during the induction period and the heat developed due to this reaction play a significant part in the occurrence of the explosion of chlorites [1]. The chemical analysis of the solid products obtained at the interruption of the heating immediately before the explosion proved the validity of this idea, as in barium chlorite 3—5%, and in lead chlorite about 2.5—5.5% chlorate was found. Accordingly, on heating the chlorites rapidly to a high temperature, the formation of chlorate sets in immediately, however, on the effect of the reaction heat, the rate of the disruption of further Cl—O bonds will increase to such an extent that there will be no possibility for the formation of new Cl—O bonds, i.e. for the stabilization of chlorite in form of chlorate. As the reaction

$$MClO_2 = MCl + O_2 \qquad (8)$$

is much more exothermic (Table II) than the disproportionation reaction, this may result in further acceleration of the reaction. This conception is proved by the thermal behaviour of barium chlorite and lead chlorite at a slow heating rate (1° C/min.). In these case explosion did not occur because the dissipation of the heat of the disproportionation reaction was secured, so chlorite completely transformed into chlorate. The chlorites failed to explode in the presence of inert substances even using a heating rate of 6° C/min. which can be explained in the same way, namely by assuming the absorption of the heat produced by the disproportionation.

Alkali chlorites, contrary to other chlorites, did not explode, what is more they did not decompose even upon the effect of the great amount of reaction heat released instantaneously when the substance had been heated at an extremely high rate. This behaviour, is, in all probability, due to the greater thermal stability of alkali chlorates compared to that of other chlorates.

In the case of silver chlorite, which is more covalent in character, it was assumed that the electron transfer reaction plays a dominant role both in the decomposition and explosion [4]

$$ClO_2^- = ClO_2 + \ominus \qquad (9)$$

$$Ag^+ + \ominus = Ag \qquad (10)$$

$$Ag^+ + n\,Ag + \ominus(n+1)\,Ag. \qquad (11)$$
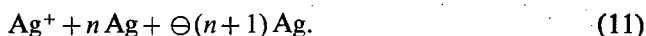
The decomposition products (ClO_2 and Ag) as well as the calculated and measured activation energies seem to support this mechanism. In the explosion of silver chlorite the reaction occurring between the silver and chlorine dioxide formed:

$$2\,Ag + ClO_2 = Ag_2O + \frac{1}{2}\,Cl_2 + \frac{1}{2}\,O_2 \qquad (12)$$
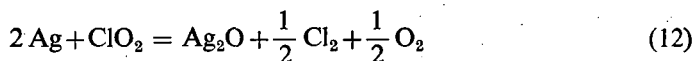
must also be taken into consideration.

F. SOLYMOSI

Thermal stability of alkali chlorates

Considerably more data are available on the thermal behaviour of chlorates than on that of chlorites. It has been observed as early as at the turn of the century that upon the effect of heat, chlorates partly disproportionated and partly decomposed. Foreign substances, especially oxides, were found to influence the direction and rate of conversion to a considerable extent.

A characteristic feature of alkali chlorates is the great temperature difference between their melting point and the initial temperature of their decomposition. A few degrees above their melting points the compounds — with the exception of cesium chlorate — underwent a decomposition of less than 1% within 2 days. Consequently, the melting points given for alkali chlorates can be considered as „congruent".

A number of workers have studied the thermal behaviour of alkali chlorates by means of differential thermal analysis, as well as by thermogravimetric, differential thermogravimetric and by combined derivatographic methods [16—20]. The most detailed investigations, extended to all of the alkaline chlorates, were carried out under the same experimental conditions by MARKOVITZ, BORYTA and STEWART [12].
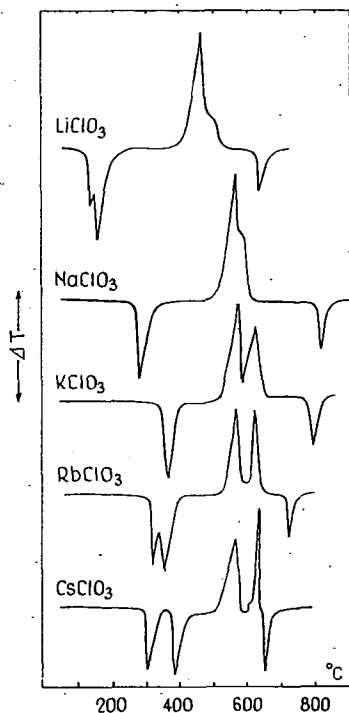

Fig. 7. DTA curves of pure alkali metal chlorates [12]. Heating rate: 4° C/min; weight of substances: 1 g
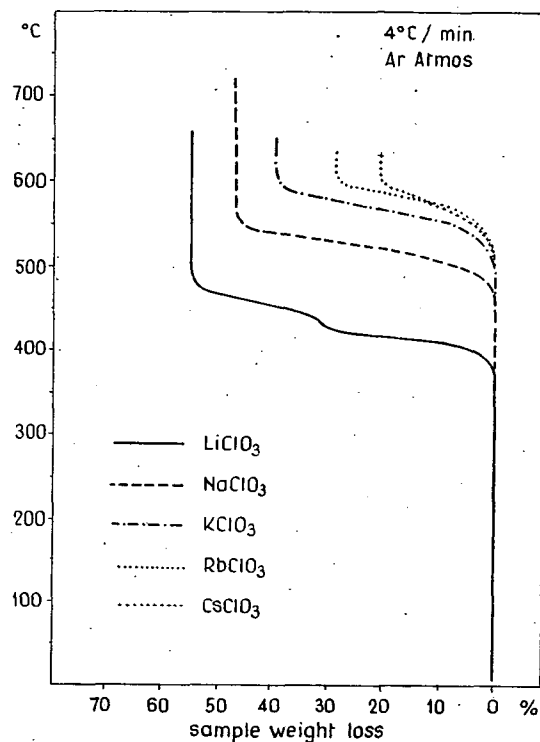
Fig. 8. Thermogram for pure alkali metal chlorates [12]. Heating rate: 4° C/min. Argon atmosphere

DTA and thermogravimetric curves obtained by these authors are given, in Fig. 7 and 8, where the first endotherm peaks correspond to the crystallographic transition as well as to melting of the substance. In the case of potassium, rubidium and cesium chlorates, two exothermic peaks can be well distinguished, while in that of lithium and sodium chlorates the exothermic peaks are obviously the results of several consecutive processes. The compositions of the samples before the appearance of the first exothermic peak are shown in Table VI. From the results of the chemical

Table VI

Composition of alkali chlorates heated to peak temperatures of first exotherms on DTA curves. Heating rate: 4°/min. [12]

| Compound	Residue composition, %			Percentage decomposition		Peak temperature °C
	$MClO_3$	MCl	$MClO_4$	to MCl	to $MClO_4$	
$LiClO_3$	0.9	68.2	30.3	57.8	40.2	425
$NaClO_3$	2.6	47.3	50.1	30.5	66.9	542
$KClO_3$	0.9	33.9	65.2	12.1	87.0	566
$PbClO_3$	1,6	32.9	65.5	11.0	87.4	563
$CsClO_3$	1.3	34.0	64.7	12.4	86.3	560

analysis it is apparent that the first exothermic peak is also the result of two simultaneously occurring reactions

$$MClO_3 = MCl + 1.5 \, O_2 \tag{13}$$

$$MClO_3 = 3/4 \, MClO_4 + 1/4 \, MCl. \tag{14}$$
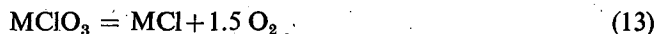
The second exothermic peak represents the decomposition of perchlorate formed during the disproportionation of chlorates. On heating lithium and sodium chlorates, the decomposition of perchlorate formed in the disproportionation commenced as soon as the first exothermic peak began to take shape.

The values of percentage weight-loss indicate that chlorine is formed practically only in the decomposition of lithium chlorate.

The extent of the reaction

$$2 \, LiClO_3 = Li_2O + Cl_2 + 2.5 \, O_2 \tag{15}$$
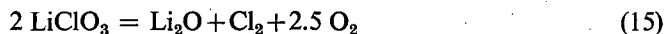
is only about 4% of the decomposition. An extremely low chlorine formation was observed in the decomposition of sodium chlorate, too.

More detailed thermogravimetric measurements revealed that an appreciable decomposition of lithium chlorate has commenced at 370° C [13]. A notable decrease in the rate of decomposition occurred at 430° C. The percentage weight-loss up to this point was 27.7% which corresponds to the reaction

$$8 \, LiClO_3 = 5 \, LiCl + 3 \, LiClO_4 + 6 \, O_2. \tag{16}$$
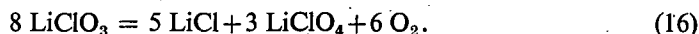
Above 430° C the decomposition of lithium perchlorate formed in the above reaction takes place at a considerably higher rate than that of pure lithium perchlorate; this may be attributed to the catalytic effect of the lithium chloride present. The

results of the measurement made at 339° C under isothermal conditions indicated that the disproportionation and decomposition of lithium chlorate practically occurs at identical rate.

Addition of lithium chloride (50 mole %) to lithium chlorate catalyzed both the decomposition and the disproportionation reaction. A significant weight-loss was observable at a temperature as low as 343° C.

The decomposition of sodium chlorate has been studied from the kinetical point of view in the temperature range between 450—480° C [18]. There is a time lag of only few minutes before the reaction. As the pressure of the oxygen evolved during the decomposition increases linearly up to $\alpha = 0.5$ with time, the rate constants of the decomposition were determined from the slope of the α-t curves. From the temperature dependence of the rate constants obtained in this way a value of 68 kcal/mole was calculated for the activation energy.

After the gas evolution had ceased, undecomposed chlorate could not be detected in the solid residue. Besides sodium chloride, however, the solid residue contained a considerable amount, (about 40 w%) of perchlorate due to the disproportionation reaction. It was attempted to separate the decomposition and disproportionation by changing the reaction temperature, but without any success.

The formation of sodium perchlorate was studied at the same temperatures. At 390° C, where the decomposition of sodium chlorate is negligible, disproportionation is also extremely slow. After 5 hours only 2.5% of sodium perchlorate was formed. On increasing the temperature the perchlorate content increased, and above 450° C it ran parallel with the decomposition.

The decomposition of potassium chlorate has also been studied under isothermal condition, mainly to find out more about the influence exerted by potassium chloride on the conversion of the compound. The opinions concerning this effect vary considerably. According to FARMER and FIRTH [21] potassium chloride did not alter the rate of formation of perchlorate, however, it accelerated oxygen evolution. The investigations of OTTO and FRY [22, 23], on the other hand, showed an opposite effect. GLASNER and WEIDENFELD [10] stated that the effect of potassium chloride depends on its pre-history. Potassium chloride, originating from the decomposition of potassium perchlorate, as well as commercial potassium chloride, treated at 600° C for 1 hour, accelerated the formation of potassium perchlorate, however, they hardly had any effect on the rate of oxygen evolution, whereas C.p. KCl dried at 110° C decreased the extent of formation of potassium perchlorate.

The activation energy of the decomposition of pure salt was calculated from the temperature dependence of the time elapsed until 20% oxygen evolution; it was found to be 54 kcal/mole [10]. Nearly identical activation energies were found from the temperature dependence of the quarter and half-times of the decomposition [24]. From the chemical analysis of the substances, pretreated at various temperatures, GLASNER and WEIDENFELD [10] came to the conclusion that perchlorate formation occurs not in a simultaneous but in a consecutive reaction.

Kinetic analysis of the decomposition of potassium chlorate has been attempted by TOBISAVA [25] without success. The failure was attributed to the complication of the rate—time curves due to irregularities of bubbling and splashing in the molten salt. According to the measurements of RUDLOFF and FREEMAN [26] the decomposition takes place in two well defined steps; one third of the theoretically calculated weight loss occurred in the first step. This part of the decomposition was described by sec-

ond order equation. The values of the activation energies of the decomposition of various chlorate-chloride mixtures were in the range between 62—66 kcal/mole. They observed that at lower temperatures, potassium chloride exerted an inhibiting effect on the decomposition of chlorate while at higher temperatures its catalytic effect became dominant. A small amount of potassium perchlorate had no effect on the decomposition however, when present in greater amounts, is shifted the commencement of the decomposition towards higher temperatures.

Thermal decomposition of other metal chlorates

Barium chlorate

A derivatogram of barium chlorate is shown in Fig. 9 [18]. The initial loss of weight starting at 146° C, and the endothermic peak at 170° C belonging to this process, are due to the loss of the one mole of crystal water. The endothermic peak indicating the melting of barium chlorate is to be found at 404° C. Simultaneously the decomposition of the substance occurs, which on increasing the temperature becomes extremely rapid, but later — in spite of the higher temperature — slows
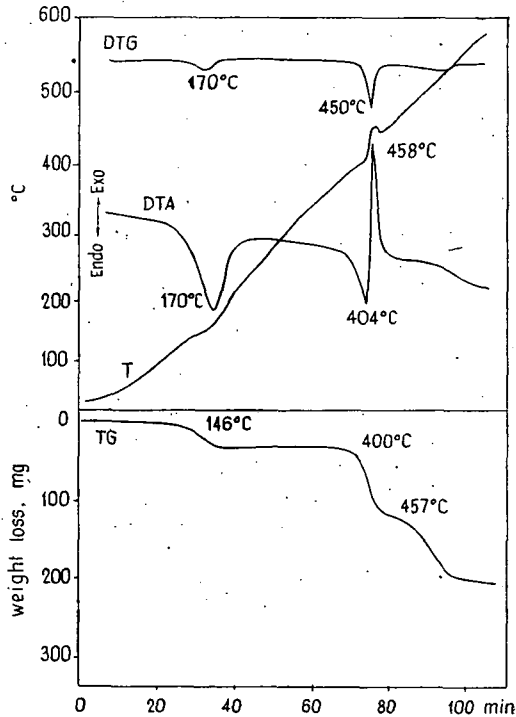

Fig. 9. Derivatogram of $Ba(ClO_3)_2$.
Heating rate: 6° C/min [18].

down again. The decomposition of barium chlorate is an exothermic process. On the basis of the analysis of samples corresponding to various parts of the derivatogram, the decomposition and the disproportionation of the substance proceeds in molten state according to the following reactions;

$$Ba(ClO_3)_2 = BaCl_2 + 3\ O_2 \tag{17}$$

$$Ba(ClO_3)_2 = 3/4\ Ba(ClO_4)_2 + 1/4\ BaCl_2. \tag{18}$$
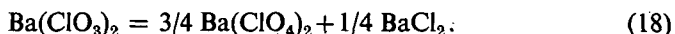
The slow weight-loss observed on the TG curve at 457° C is the result of the decomposition of the perchlorate formed

$$Ba(ClO_4)_2 = BaCl_2 + 4\ O_2. \tag{19}$$

The measurements made under isothermal conditions gave similar results [27, 18]. At temperatures below the melting point the rate of the decomposition is extremely slow. However, as the temperature was getting near to the melting point (around 396° C) the behaviour of the substance suddenly changed and the rate of its decomposition became very rapid.

In spite of the rapid decomposition of the substance disproportionation also takes place. After about 70—80% decomposition the rate of gas evolution considerably decreased. According to visual observations the cessation and the considerable decrease in the rate of gas evolution, respectively coincided with the solidification of the reacting system.

However, the solidification of the system alone does not seem to be a sufficient reason for the great rate decrease, since the solid substance decompose even at 380° C. It is more probable that the glass-like state of the substance also plays a part in the greater stability of the solidified melt; its surface and porosity markedly differ from those of the initial solid substance.

For the kinetic analysis of the pressure-time curves, the PROUT—TOMPKINS relation proved to be most suitable. Owing to the considerable scattering of the rate constants, the activation energy of the decomposition could not succesfully be determined, thus as an approximate value of 75 kcal/mole was given.

Silver chlorate

On the DTA curve of silver chlorate endothermic peaks can be found at 164 and 252° C (Fig. 10). The exothermic heat change accompanying the decomposition of the compound occurs at 340° C. The first and the second endothermic peaks correspond to the loss of the adsorbed water and to the melting of the compounds, respectively [28]. The decomposition of silver chlorate commences well above its melting point and takes place according to the reaction

$$AgClO_3 = AgCl + 1.5\ O_2. \tag{20}$$

The amount of chlorine and chlorine dioxide was not more than 2—3 per cent of the gas evolved.

Kinetic investigations were made in the temperature range 316—339° C [4, 28]. The reaction took place according to the first order equation (up to $\alpha = 0.9$); the value of activation energy was 57.1 kcal/mole. Simultaneously with the decomposition of chlorate, disproportionation of the compound also occurred to a small extent (8—10%). In contrast to earlier findings [29], the explosion of silver chlorate was not observed even at temperatures as high as 400—450° C.
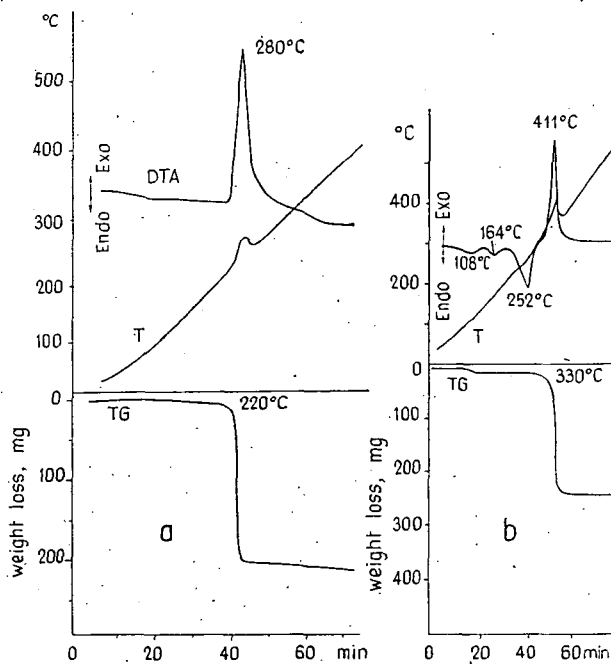

Fig. 10. Derivatogram of Pb(ClO₃)₂ (a) and AgClO₃ (b). Heating rate: 6° C/min. [18]

Lead chlorate

Thermogravimetric measurements indicate that lead chlorate begins to decompose at 220° C, and that the highly-exothermic decomposition is complete within a few seconds [18] (Fig. 10). The weight loss is 37.2%. Under isothermal conditions the reaction takes place completely at 194—216° C, with a weight loss of 35.2%. The solid residue was found to contain 84.39% PbO_2 and 14.9% $PbCl_2$. Their molar ratio is 6.58. On the basis of the reaction products the decomposition of lead chlorate can be characterized by the following overall equation;

$$8\ Pb(ClO_3)_2 = 7\ PbO_2 + PbCl_2 + 5.5\ Cl_2 + 3\ ClO_2 + 14\ O_2. \tag{21}$$
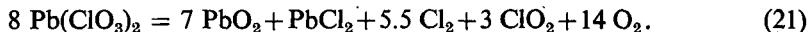
According to the equation, the weight loss is 34.8%, and the $PbO_2 : PbCl_2$ molar ratio is 7. The experimentally found $Cl_2 : ClO_2$ molar ratio likewise corresponds to the above reaction equation.

The pressure-time curve of the decomposition of lead chlorate is markedly different from that of other compounds (Fig. 11). The decomposition begins (after a heating period of a few minutes) without a time lag, and the following stages can be distinguished:

(a) an initial fast decomposition of a deceleratory nature;
(b) the subsequent slow reaction;
(c) an extremely fast decomposition, in which about two thirds of the material decomposes;
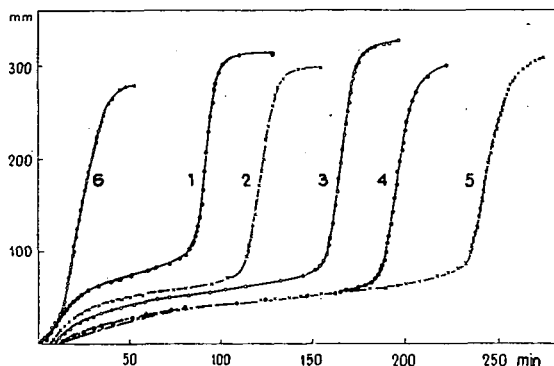(d) a short, slow decay period.

Fig. 11. Pressure *vs.* time curves of the decomposition of Pb(ClO$_3$)$_2$ [18]. (*1*) at 216° C; (*2*) at 212° C; (*3*) at 207° C; (*4*) at 203° C; (*5*) at 119.5° C; (*6*) Pb(ClO$_3$)$_2$ + solid residue of decomposition, weight ratio 5:1, at 207° C

Decomposition curves of a similar nature resulted from the measurement of the pressure of oxygen, and of the change of weight of the sample. This showed that the sudden increase in pressure during the progress of the reaction is not a result of the decomposition of the chlorine dioxide already formed, but a characteristic property of the solid-phase decomposition of lead chlorate.

It is likely that the initial rapid decomposition is a surface reaction, which penetrates to some depth into interior of the crystal. The decomposition in the bulk actually occurs in the third very fast reaction, which is preceded by a long constant rate process. This can be regarded as an induction period of the former reaction. It was assumed that the decomposition in the third stage takes place at the interface between the salt and the products. This idea was supported by the effect of the reaction product (Fig. 11). In this case the slow constant rate process between the initial and the subsequent rapid reactions practically disappeared.

The first deceleration stage followed the monomolecular decay equation. The value of the activation energy was 51.2 kcal/mole. Analysis of the slowly accelerating decomposition following the first stage showed that the kinetics satisfied both the PROUT—TOMPKINS and the AVRAMI—EROFEYEV equations. The activation energy for this stage was 43.1 kcal/mole. The rate of decomposition of lead chlorate in the third stage was practically independent of temperature.

In contrast with the chlorates discussed above, experiments carried out at the decomposition temperature or below indicated that the lead chlorate did not disproportionate at all. At a higher temperature, 246° C, the substance (50 mg) exploded. The explosion was preceded by a well-measurable decomposition. The composition of the gas product was 84.5% O_2 and 15.2% Cl_2. The temperature-dependence of the induction periods of the explosion between 246 and 260° C gave an activation energy of 64.9 kcal/mole.

Thallium chlorate

The derivatograms of thallium chlorate show that the decomposition commences at 195° C and is accompanied by the evolution of much heat [18]. (Fig. 12). The second stage of the thermogram corresponds to the evaporation of TlCl, while in the third stage the decomposition of Tl_2O_3 occurs; both compounds are formed in the decomposition of $TlClO_3$.
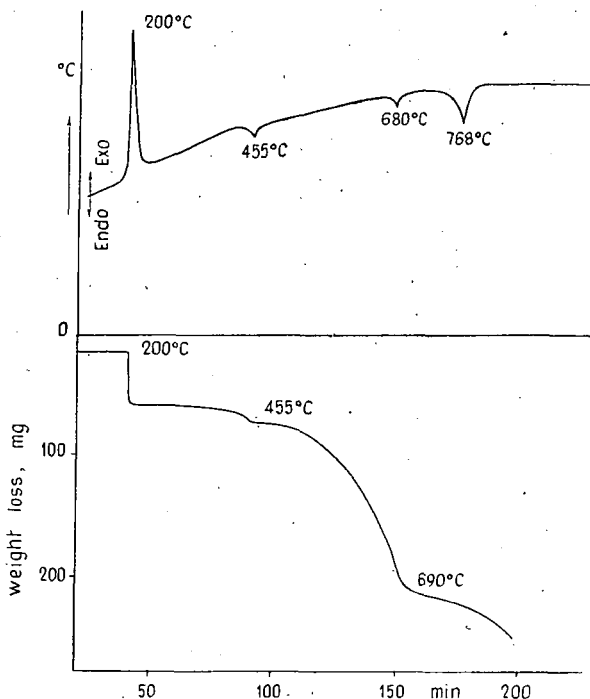

Fig. 12. Derivatogram of $TlClO_3$. Heating rate: 6° C/min [18]

Kinetic measurements were carried out at 150—170° C by measuring the decrease of weight of the sample. The gaseous products of the decomposition were completely frozen out by liquid air, showing that oxygen was not formed during the decomposition. The frozen-out gas was chlorine dioxide. In the course of the decomposition 21—26% of the material was converted to gaseous products. The

residual solid consisted of 85.63 % Tl_2O_3 and 14.23 % $TlCl$. The Tl_2O_3 : $TlCl$ molar ratio was 2.93. The solid material did not contain undecomposed thallium chlorate or thallium perchlorate.

Based on the above data, the overall equation for the decomposition of thallium chlorate is:

$$7\ TlClO_3 = 3\ Tl_2O_3 + TlCl + 6\ ClO_2. \qquad (22)$$
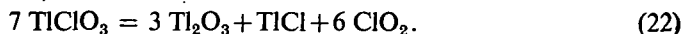
Accordingly the weight loss is 20.09 %, and the Tl_2O_3 : $TlCl$ molar ratio is 3.

The PROUT—TOMPKINS equation proved suitable for the description of the decomposition in the range $\alpha = 0.09$—0.9. The decomposition was also described excellently by the AVRAMI—EROFEYEV relation in the range $\alpha = 0.07$—0.95. The temperature dependence of the rate constants gave an activation energy of

Table VII

Kinetic data for the decomposition of metal chlorates

Compound	Temperature range °C	Methods	Activation energy kcal/mole	Frequency factor (min⁻¹),	Kinetic equation	Validity α=
$NaClO_3$	457—478	vacuum, O_2 pressure	68.6	$8.61 \cdot 10^{17}$	slope of p—t curves	0.0—0.55
	457—478	vacuum, O_2 pressure	70.9	$2.29 \cdot 10^{18}$	first-order	0.01—0.65
	457—478	vacuum, O_2 pressure	67.6	$5.77 \cdot 10^{17}$	first-order	0.65—0.95
$KClO_3$	460—500	in air O_2 ml	53.9	—	time for 10 ml O_2	—
	460—500	in air O_2 ml	52.5	—		—
	455—575	in air O_2 ml	54.0	—	Time elapsed until 20% of decomposition	
$KClO_3 + KCl$ 1:1	538—605	in air weight-loss	64.9	—	half-time $\tau_{1/2}$	
$Ba(ClO_3)_2$	380—405	vacuum O_2 pressure	75.0	—	Prout-Tompkins	
$AgClO_3$	316—339	vacuum, O_2 pressure	57.1	$1.0 \cdot 10^{19}$	first-order	0.2—0.7
$Pb(ClO_3)_2$	195—216	vacuum O_2 pressure	51.2	$1.81 \cdot 10^{21}$	first-order	
			43.1	$4.14 \cdot 10^{17}$	Prout-Tompkins induction period	
	246—260 explosion	in air O_2 ml	64.9	—		—
$TlClO_3$	150—171	vacuum weight-loss	34.5	$4.15 \cdot 10^{15}$	Prout-Tompkins	0.09—0.9
			36.6	$1.56 \cdot 10^{15}$	Avrami-Erofeyev n=3	0.07—0.95
			34.1	—	rate max.	

35.5 kcal/mole. When the thallium chlorate was mixed in advance with the solid
residue, the decomposition began sooner and took place at a higher rate. If the
gaseous products were removed continuously, or the experiments were carried out
at atmospheric pressure, the course of the decomposition remained essentially
unchanged. The solid reaction products showed a catalytic effect in this case, too.

Similarly to lead chlorate, on heating to a higher temperature thallium chlorate
exploded. The explosion here was much milder than in the previous case. An ex-
plosion-like reaction first appeared at 196° C. The induction period was about
5 minutes. With the increase of the temperature the induction period decreased,.
but the violence of the explosion did not vary.

Table VII summarizes the kinetic data of the decomposition of chlorates.

### Mechanisms of decomposition and disproportionation of the chlorates

Because of the small number of kinetic studies and the possibility of parallel
reactions, the evaluation of the mechanisms of the conversion of chlorates is fairly
difficult. Although it has not proved possible so far to detect chlorite during the
decompositions of the chlorates, it appears probable that the oxygen is not split
off in a single step, but progressively, and that chlorite is formed as an intermediate:

$$ClO_3^- = ClO_2^- + O. \tag{23}$$

In the following step the chlorite can react in one of two ways, either decomposing
to chloride:

$$ClO_2^- = Cl^- + O_2 \tag{24}$$

or disproportionating to chlorate and chloride:

$$ClO_2^- = \frac{2}{3} ClO_3^- + \frac{1}{3} Cl^-. \tag{25}$$
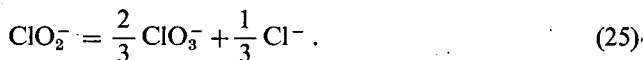
Experiments with alkali metal chlorites, already described in detail above, showed
that in the absence of catalysts only the latter reaction need to be taken into con-
sideration, even at high temperature. At the temperature of decomposition of the
chlorates, however, barium and silver chlorites no longer disproportionate, but
decompose. Since both processes occur instantaneously at the temperature of de-
composition of the chlorates, *the rate-determining step in the decomposition of the
chlorates is at any event the first reaction, which means the rupture of the Cl—O bond.*
The values of activation energy determined experimentally so far practically agree
with the energy value necessary for breaking off the Cl—O bond. This explanation
is supported by the values of the reaction heat calculated for reaction 23 (Table VIII)
which, assuming the formation of atomic oxygen, agree well with the activation
energy values determined for the decompositions of sodium, potassium and silver
chlorates. It is very likely that this reaction mechanism also holds for the decomposi-
tions of the other metal chlorates giving chloride and oxygen.

In addition to the above decomposition mechanism, we may consider the
possibility that the decompositions of chlorates proceed *via* an electron-transfer
mechanism. In this case the rate-determining step should be the reaction

$$M^+ + ClO_3^- = M + ClO_3 \tag{26}$$

Table VIII

Equivalent heat of reaction for different transformations of chlorates

Compound	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6
$LiClO_3$	−27.70	−1.2	−23.2	—	−21.7	—
$NaClO_3$	−12.5	+36.0	−8.1	+9.08 (+68.28)*	−8.5	+1.31
$KClO_3$	−10.675	+50.3	−10.24	—	−10.1	—
$RbClO_3$	−9.11	+54.35	−9.85	—	−10.1	—
$CsClO_3$	−7.5	+58.05	−7.80	—	−7.9	—
$Ba(ClO_3)_2$	−11.93	+24.35	−7.14	+11.75 (+70.95)*	−5.55	+3.1
$AgClO_3$	−24.57	+2.47	−7.67	+5.73 (+64.93)*	−2.02	+1.86

1. $MeClO_3 = MeCl + 1.5\ O_2$
2. $MeClO_3 = \frac{1}{2}Me_2O + gases$
3. $MeClO_3 = \frac{3}{4}\ MeClO_4 + \frac{1}{4}\ MeCl$
4. $MeClO_3 = MeClO_2 + \frac{1}{2}\ O_2$ (or O)
5. $MeClO_3 + \frac{1}{2}\ O_2 = MeClO_4$
6. $MeClO_3 = \frac{1}{2}\ MeClO_4 + \frac{1}{2}\ MeClO_2$

* Assuming the formation of atomic oxygen in reaction 4.

i.e. the formation of the chlorate radical. In the case when the necessary data (absorption edge, dielectric constant and refractive index values) were known, the activation energy (E_T) required for the electron-transfer process has been calculated (Table IX). These activation energy values lie fairly close to those experimentally

Table IX

Some data for the structure and physical properties of chlorates

Compound	Crystal transition point °C	Melting point °C	Density	Refractive index	Dielectric constant at 350 kc/s K	K_0/K	Absorption edge $\overset{\circ}{A}$	E_0 eV	E_T eV	Ionic character %
$LiClO_3$	111	129	2.631							67.64
$NaClO_3$		263	2.490	1.515	5.9	0.389				68.7
$KClO_3$		357								73.0
$RbClO_3$	323	342	3.184							
$CsClO_3$	305	388	3.626							
$Ba(ClO_3)_2$		404	3.179	1.577	4.34	0.573				45.2
$AgClO_3$		232	4.430	1.83	5.81	0.575	2550	4.86	2.79	36.0
$Pb(ClO_3)_2$		decomp.	5.047		11.78		2380	5.21		17.1
$TlClO_3$		decomp.	4.047		7.78		2420	5.12		25.2

$K_0 = n^2$
$K_0 =$ high frequency dielectric constant
$K\ =$ low frequency dielectric constant
$n\ =$ refractive index
$E_0 =$ optical activation energy
$E_T =$ thermal activation energy

determined. However, in our view the electron-transfer mechanism does not play an essential role in the decomposition of chlorates, since chlorine and chlorine dioxide would be formed at any rate from the decomposition of the chlorate radicals, or from the interaction of the chlorate radical and the alkali metal. Chlorine however was formed only in negligibly small quantity in the course of the experiments. Nevertheless, it is not possible to exclude completely the electron-transfer mechanism in the cases of lead and thallium chlorates; though data for the calculations are lacking here.

In the treatment of the disproportionation of chlorites, a detailed account has already been given of the different views relating to the disproportionation of the oxyanions of chlorine. Although the experiments of BOSCH and ATEN [11] using potassium chloride containing labelled chlorine, excluded the formation of perchlorate in a reaction between the alkali metal chloride and atomic oxygen, a reaction of a similar type has recently been assumed between barium chloride and atomic oxygen [30]. However, taking into account the stabilities of the assumed intermediates $Ba(OCl)_2$ and $Ba(ClO)_2$ at the temperature of decomposition of barium chlorate, in our opinion this reaction path is very improbable. According to the thermodynamic data given in Table VIII, the oxidation of the chlorates, similarly to that of the chlorates, is thermodynamically possible with molecular oxygen, but kinetically the reaction does not occur, even at high oxygen pressures and high temperatures. As a result, the formation of perchlorate is due either to the reaction between chlorate and the atomic oxygen formed during the decomposition of chlorate:

$$MClO_3 + O = MClO_4 \qquad\qquad (27)$$

or, similarly to the disproportionation of chlorites, to intermolecular rearrangement. To find decisive evidence for or against the mechanisms is very difficult. In any case it is probable that the disproportionation of chlorites and chlorates proceeds for similar reasons and in essentially the same way. Detailed kinetic measurements made in the case of the chlorites, and also certain other observations mentioned there, seem to contradict to the oxidation with atomic oxygen.

Similarly to the transformations of the chlorites, the disproportionations of both sodium and barium chlorate began prior to perceptible decomposition. With the oxidation mechanism this result can be explained only by the circumstance that the rate of oxidation of chlorate is much higher than the rate of recombination of oxygen atoms:

$$O + O + surface = O_2 + surface$$
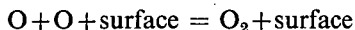
which cannot be ruled out because of the low concentration of oxygen atoms. In our view the intermolecular rearrangement is supported by the values of the reaction heats given in Table VIII. According to the oxidation mechanism, the rate-determining step in the perchlorate formation is in all probability the rupture of a Cl—O bond of the chlorate ion (formation of atomic oxygen), i.e. the same reaction step as the rate-determining process of the decomposition. The reaction heat of the process has a fairly high value of 65—70 kcal/mole (see Table VIII), in good agreement with the values of the activation energy determined experimentally for the decompositions.

7

The simplest means of intermolecular rearrangement is an interaction between two chlorate ions, in the course of which one molecule of perchlorate and one molecule of chlorite are formed:

$$2\,ClO_3^- = ClO_4^- + ClO_2^-. \qquad (28)$$

This chlorite rapidly disproportionates, with the formation of chlorate and chloride. Taking into account the considerations given in the discussion of the disproportionation of the chlorites, in the optimum case the activation energy of the disproportionation reaction will be equal to the difference of the two dissociation energies, that is the reaction heat, which can be seen from Table VIII to be endothermic by only a few kcal/mole. It is probable that in reality this optimum case does not hold, but on the above basis it seems very plausible that, in contrast with the oxidation of the chlorate, this reaction path is energetically substantially more favourable. A reaction mechanism agreeing many respects with that described earlier by us [18] was recently put forward by RUDLOFF and FREEMAN [26] for the disproportionation of potassium chlorate. It was assumed that the potassium perchlorate was formed by *direct oxygen transfer between two chlorate anions*. In accordance with the second-order kinetics, the potassium chlorate is first transformed in a slow reaction to potassium perchlorate and chlorite:

$$2\,KClO_3 = KClO_4 + KClO_2, \qquad (29)$$
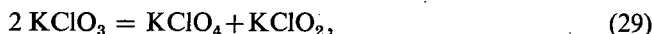
the potassium chlorite formed as an intermediate decomposing rapidly:

$$KClO_2 = KCl + O_2. \qquad (30)$$

Their assumption that the potassium chlorite immediately decomposes to chloride and oxygen, however, is in contradiction with the thermal behaviour of alkali metal chlorites. As was pointed out earlier, the alkali metal chlorites do not decompose at even higher temperature, but disproportionate to chlorate. Accordingly the transformation of potassium chlorate into perchlorate and chlorite does not result in the formation of oxygen below the decomposition temperature of potassium perchlorate. The rate-decreasing effect of potassium chloride observed at lower temperature was explained by RUDLOFF and FREEMAN by the decrease of the probability of approach of the chlorate anions. The catalytic effect of the potassium chloride at higher temperatures was interpreted by the formation of polarizing centres in the melt. These polarizing centres may influence the electron shells of the oxygens of the chlorate and perchlorate anions.

The mechanisms of decomposition of chlorates which give rise predominantly to oxide formation is much more complex than that of alkali chlorates. An interesting fact in the decompositions of both salts investigated in more detail (lead and thallium chlorates) is that the metal ions were oxidized. This may occur in two ways: either by the molecular or atomic oxygen produced in the decomposition of the chlorate, or by means of internal oxidation within the crystal. The activation energy values are lower than the dissociation energy of the Cl—O bond, or in other words, than the energy necessary for the formation of atomic oxygen. This is in agreement with the fact that in both decompositions the chloride formation is about 6—7 times slower than that of the oxide formation. In our opinion, it is probable that Tl_2O_3 and PbO_2 are formed in intramolecular rearrangements, together with the production

of chlorine dioxide, which at the temperature of decomposition of lead chlorate partially decomposes on the solid residue to oxygen and chlorine.

In these cases perchlorate was not formed. This cannot be accounted for by decomposition of the compounds in the solid phase, since in the solid disproportionation of the chlorites does take place. It is much more probable that during an internal rearrangement the formation of the oxide of the metal of higher valency is associated with a substantially greater free energy decrease than that for the formation of the perchlorate. Due to the lack of the free enthalpies of formation of these chlorates and perchlorates, this assumption can not be confirmed for the time being. In addition it must be taken into consideration that in the decomposition of both chlorates metal oxide was formed. In the presence of the metal oxides, however, instead of the disproportionation of the chlorates the decomposition reaction predominates.

Although the investigations to date have been extended to relatively few substances, by considering the physical properties and bonding relations of the compounds and the characteristics of the cations (Table IX) it can be stated that the more ionic the compound, or the smaller the effective electric field strength (polarizing power) of the cations, the higher the temperature at which the compounds begin to decompose. There does not exist such a clear-cut relation for the disproportionation of the compounds. In the case of compounds of similar character, namely the alkali metal compounds, a reverse relation holds: the decrease of the ionic character, or the increase of the polarizing power of the cation, favours the formation of the oxyanions of chlorine with higher oxygen content. In the series, alkali metal — barium — silver — lead compounds, however, the finding for the decompositions also refers to the disproportionations.

### Thermal stability of alkali metal perchlorates. Thermal analysis

Although the thermal decomposition of the alkali metal perchlorates has already been studied before the turn of the century, and many observations were made which are still valid, nevertheless a significant advance in evaluating the thermal stabilities of these compounds was achieved only after the preparation of compounds of suitable purity and after the introduction of modern thermal analytical and kinetic methods. Thermogravimetric measurements and differential thermal analysis of solid perchlorates were carried out first by MARVIN and WOOLAVER [31], and then by GORDON and CAMPBELL [32]. These methods were later used by numerous authors, particularly in the study of the alkali metal compounds [17, 33—35]. A detailed thermal analytical investigation extended to each member of the group, under identical experimental conditions, was performed by MARKOVITZ et al. [36—40], and by SOLYMOSI [35, 41]. The characteristics of their DTA curves [19] are shown in Fig. 13. With the exception of lithium perchlorate, the first endothermic peak in each of the DTA curves signifies the reversible transition from the rhombic to the cubic modification. The second endothermic peak is a result of the melting of the relevant substance and the exothermic peak belongs to the decomposition. In the case of lithium perchlorate, and, to a lesser extent, in the case of sodium perchlorate, too, the melting is well separated from the decomposition, whereas in the other cases the decomposition occurs immediately after the melting begins. The endothermic.

peak at higher temperature results from the melting of the chloride formed in the decomposition of the perchlorate.

Thermogravimetric examinations (Fig. 14) indicate that the alkali metal perchlorates decompose in accordance with the basic equation

$$MClO_4 = MCl + 2\,O_2. \tag{31}$$

Oxide and chlorine formation:

$$MClO_4 = 0.5\,M_2O + 1/2\,Cl_2 + 3.5\,O_2 \tag{32}$$
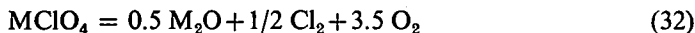
was observed only in the decomposition of lithium perchlorate. Even here, however, the amount of chlorine evolved did not exceed 2% of the chlorine in the perchlorate.
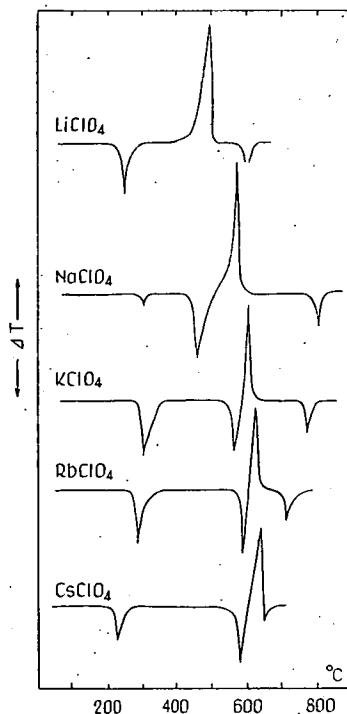

Fig. 13. DTA curves for alkali metal perchlorates. Heating rate: 4°/min. 1 g sample; Ar atmosphere [40]

The derivatographic method was used for a detailed study of the effects of the corresponding chlorides on the thermal behaviours of the alkali metal perchlorates [35]. With the exception of the lithium system, the chlorides markedly decreased the temperatures at which the alkali metal perchlorates melted and also the temperatures of the commencement of decomposition. Fig. 15 illustrates this effect in the case of $RbClO_4$—$RbCl$ system. The characteristic data concerning the effect of
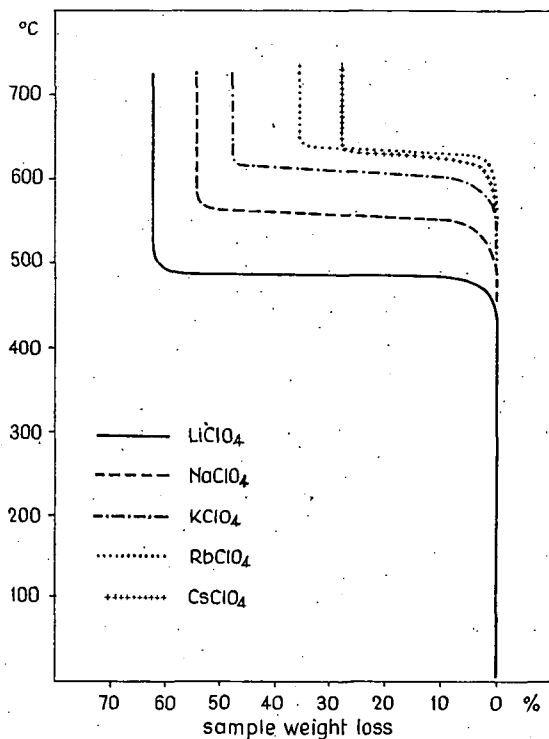
Fig. 14. TGA curves for pure alkali metal perchlorates.
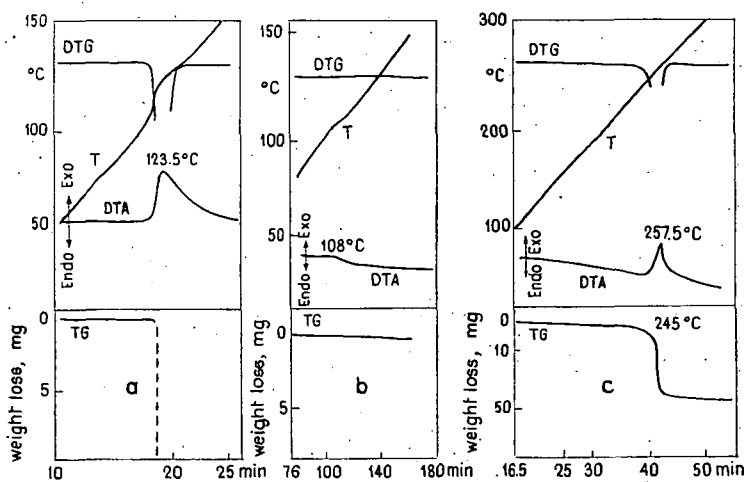Heating rate: 4°/min; Ar atmosphere [40]

Fig. 15. Derivatograms of RbClO$_4$. Heating rate: 6°/min. (a) Pure RbClO$_4$;
(b) RbClO$_4$:RbCl, 50:50; (c) RbClO$_4$:RbCl, 70:30 mole% [35]

Table X

Thermal behaviour of alkali perchlorates in the presence of alkali chlorides. Derivatographic investigation [35]

LiClO$_4$:LiCl mole %	Melting point °C	t °C*	NaClO$_4$: NaCl mole %	Melting point °C	t °C*	KClO$_4$:KCl mole %	Melting point °C	t °C*
100:0	247	450	100:0	471	507	100:0	570	550
90:10	243	420	90:10	428	500	90:10		
70:30	246	390	70:30	415	485	70:30	508	508
50:50	251	390	50:50	423	485	50:50	523	510

RbClO$_4$: RbCl mole %	Melting point °C	t °C*	CsClO$_4$: CsCl mole %	Melting point °C	t °C*
100:0	610	600	100:0	571	570
90:10			90:10	500	480
70:30	489	500	70:30	447	460
50:50	490	490	50:50	550	500

* Temperature of the onset of decomposition
  Heating rate 6°/min.

alkali chlorides are collected in Table X. The addition of lithium chloride to lithium perchlorate hardly affected its melting point, but it exerted a large catalytic influence on the decomposition of the perchlorate.

More details concerning the nature of the decomposition of alkali perchlorates have been disclosed by kinetic investigations.

Kinetic studies

Lithium perchlorates

The kinetic study of the thermal decomposition of lithium perchlorate was first dealt with by MARKOVITZ and BORYTA [42]. The decomposition began only above 380° C and proceeded to the end in molten phase. The reaction is of auto-catalytic nature; the decomposition is preceded by a fairly long time lag. The above authors found the PROUT—TOMPKINS equation and the monomolecular decay equation to be suitable for the mathematical analysis of the decomposition curves. For the activation energies of the acceleration and breakdown stages as 52.2 and 62 kcal/mole, respectively, were obtained. The transition between the two rate laws was explained by the saturation of the perchlorate melt with lithium chloride.

Detailed measurements were carried out to detect possible intermediates in the decomposition. Lithium chlorate was found already at $\alpha=0.1$; its amount increased up to $\alpha=0.5$ (2%), but at higher values of α it decreased. Lithium chlorite could not be detected in any single case.

The phase-diagram of the LiClO$_4$—LiCl system was studied in detail by means of differential thermal analysis and visual observations. It was concluded from the results obtained that the system is of simple eutectic type, and that the composition of the eutectic contains 91 mole % LiClO$_4$.

Lithium chloride exerted a significant catalytic effect on the decomposition. In the presence of 5 mole % LiCl the decomposition began without a time lag, while 50 mole % LiCl changed the autocatalytic reaction to a deceleratory one. The addition of lithium chloride did not affect either the values of the rate constants or the activation energy of the decomposition. It was assumed, however, that the activation energy value mentioned above could be considered as that of the reaction affected by the lithium chloride formed in the decomposition. In agreement with this, from the temperature-dependence of the times elapsed up to a decomposition of only 0.5% the above authors obtained a higher activation energy value of 58.3 kcal/mole.

The catalytic effect of lithium chloride was supported by the results obtained using silver nitrate or silver perchlorate additives [43]. The decomposition of pure lithium perchlorate at 417.8° C was complete within a few hours. The presence of silver nitrate increased the stability of the compound to a considerable extent, and the time lag exceeded 30—35 hours. The phenomenon is clearly related to the insolubility of solid silver chloride in lithium perchlorate, and to the loss of the chloride catalyst. According to DTA investigations, however, at 455° C, the melting point of silver chloride, the decomposition of lithium perchlorate containing the silver ion becomes very rapid; this is presumably caused by the entry of the chloride ion into the solution during the melting of the silver chloride.

The decomposition of the compound was later studied by measuring the pressure of the O_2 evolved [35, 44]. Using the previous kinetic equations, a value of 52.6 kcal/ mole was obtained for the activation energy of the acceleration stage, while the value for the decay stage, 41 kcal/mole, was significantly less than the value determined earlier.

Sodium perchlorate

The decomposition of sodium perchlorate was studied kinetically first by BENARD and CABANE [45] in the range 330—428° C, that is below the melting point of the compound. Because of the extremely slow decomposition the reaction time exceeded several hundred hours, and even then the decomposition amounted to only a few percent. The authors determined the self-diffusion constant of the perchlorate ion, and also its temperature coefficient. Identical activation energies of 27—28 kcal/mole were obtained for the thermal decomposition and for the diffusion of the perchlorate ion.

The complete decomposition of sodium perchlorate proceeds with a measurable rate in the range 490—515° C [35, 44]. The reaction is of autocatalytic nature. The rate maximum is shifted towards a later stage of the decomposition by the increase of the reaction temperature. The decomposition is preceded by a time lag of a few minutes, which is practically independent of the temperature. The reaction proceeds completely in the direction of chloride formation. The α vs. t curves were well described by the PROUT—TOMPKINS relation. The activation energies of the acceleration and decay stages were found to be 57.3 and 57.0 kcal/mole, respectively. The first-order formula, too, was suitable for the mathematical analysis of the breakdown stage.
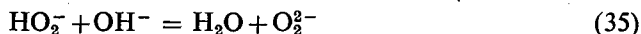
The decomposition began with maximum rate and the half-time of the reaction was decreased considerably by the preliminary addition of sodium chloride to the sodium perchlorate.

Very interesting results were obtained by the study of the decomposition of sodium perchlorate in a sodium hydroxide melt [46]. At 360—420° C the decomposition proceeded about 10^4 times faster than in the case of the pure perchlorate. In the first part of the reaction chlorate was formed, and this slowly decomposed to chloride and oxygen. The first reaction was about 12—18 times faster than the second process. The interesting observation was made that starting from sodium chlorate the disproportionation of the chlorate in a sodium hydroxide melt remained below 0.5%. It is questionable whether this is due to the lower temperature (which is not very probable), or to change in the decomposition mechanism.

Both reactions can be described by first-order kinetics. The activation energy values for the two reactions were 47.3 and 53.2 kcal/mole, significantly lower than those determined for the decompositions of pure perchlorate and chlorate. The accelerating effect of hydroxide ion was interpreted by assuming of the reaction steps.

$$ClO_4^- + OH^- = ClO_3^- + HO_2^- \tag{33}$$

$$ClO_3^- + OH^- = ClO_2^- + HO_2^- . \tag{34}$$
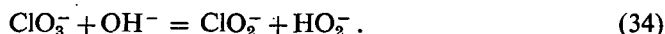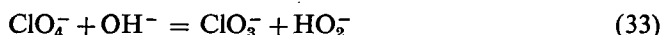
The HO_2^- formed reacts with OH^-:

$$HO_2^- + OH^- = H_2O + O_2^{2-} \tag{35}$$

and the peroxide formed is transformed as follows:

$$2 O_2^{2-} + 2 H_2O = O_2 + 4 OH^- . \tag{36}$$
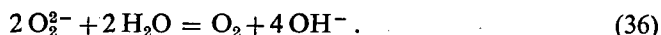
Accumulation of chlorite and hypochlorite was not observed, and this was explained by the rapid decomposition of the chlorite to chloride. This would mean that the direction of the transformation of sodium chlorite changes in a melt containing hydroxide ions, since measurements showed that $NaClO_2$ in the solid phase disproportionates without decomposition even at a higher temperature. This can be thought to proceed similarly as above:

$$ClO_2^- + HO^- = ClO^- + HO_2^- \tag{37}$$

$$ClO^- + HO^- = Cl^- + HO_2^- \tag{38}$$
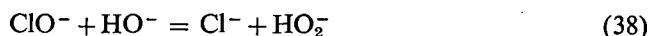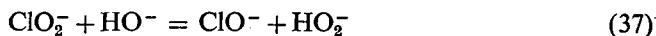
The probable cause of the absence of disproportionation is the high affinity of oxyanions of chlorine for the hydroxide ion.

It emerged from a study of the effects of various additives that water, sodium peroxide, magnesium oxide and barium oxide exert only slight effects on the reactions.

Potassium perchlorate

The decomposition of potassium perchlorate was first investigated from a kinetic aspect by OTTO and FRY [47]. The reaction followed the first-order rate law. Chlorate was not observed as intermediate. According to HOFFMANN and MARIN [48], however, a partially decomposed perchlorate sample contained 14.55 weight% chlorate.

The first thorough studies were carried out by GLASNER et al. [49, 50] in vacuum and at atmospheric pressure. Although the compound melted during the decompo-

sition, the authors came to the conclusion that the reaction was independent of the physical state of the system and proceeded in accordance with the characteristics of a process of the type

$$solid_A \rightarrow solid_B + gases. \tag{39}$$

It was further assumed that the molten phase can be regarded as quasicrystalline. The kinetic analysis of the reaction was performed with the modified PROUT—TOMPKINS equation. It was assumed that the decomposition of potassium perchlorate takes place according to two different basic processes [51]. The first, a fairly slow reaction, corresponds to the initiation of the decomposition, while the second, 500 times faster than the former, is the propagation of the decomposition by a chain-branching mechanism.

The applicability of the PROUT—TOMPKINS equation was later questioned by BIRCUMSHAW [52] who was the first to point out the extremely complex nature of the reaction. His main findings were as follows:

1. The solid-phase decomposition is accompanied at first by the formation of potassium chlorate and potassium chloride. The latter accelerates the reaction, and as a consequence of the accumulation of the potassium chlorate the system melts.

2. The melt-phase decomposition begins only on completion of the transition into the melt phase.

3. Accumulation of the potassium chloride leads to solidification of the melt and to slowing-down of the gas evolution.

HARVEY et al. [53] studied the decomposition of potassium perchlorate under the pressure of oxygen formed in static vacuum. It was observed that the decomposition rate depends on the concentration of the perchlorate and on the physical state of the reacting substance. This is shown in Fig. 16 where the data of four experiments at different temperatures are presented by plotting of $\log/P_f - P_t/vs.$ time. P_f is the pressure of oxygen calculated for complete decomposition of the sample, P_t is the experimentally measured pressure at time t.

On the curves the points referring to the first phase change, to the end of melting and to the appearance of second solid phase calculated from phase diagram are also indicated. The decomposition can be described by two first-order equations before the appearance of the second solid phase; one of these equations refers to the initial slow decomposition in the solid phase, and the other to the subsequent rapid decomposition in the melt. (At the transition of the solid phase into the melt phase the reaction occurs in both phases.) The rate constant for the liquid-phase decomposition is about 50 times larger than that for the solid phase. The temperature-dependence of the rate constants was however, the same, and the value of the activation energy was 70 kcal/mole; it was concluded, therefore that the mechanism of the decomposition was the same in both phases. Potassium chlorate was found as intermediate only to the extent of 2—3%.

In the experiments of RODGERS and WASSINK [54] the activation energies of the reactions proceeding in the two phases differed by 18 kcal/mole. The most recent measurements of the author [35, 44], however, support the results of HARVEY et al.

They found that the rate and activation energy of the decomposition are practically independent of the pressure of the oxygen, and it was concluded that the oxygen does not participate in an equilibrium reaction [55]. However, as will be clear later, this refers only to molecular oxygen.

The investigations reported in the case of sodium perchlorate were extended by CABANE and BENARD [45] also to potassium perchlorate. The activation energies of the thermal decomposition and the self-diffusion of the perchlorate ion (30—32 kcal/mole) agreed well here, too.
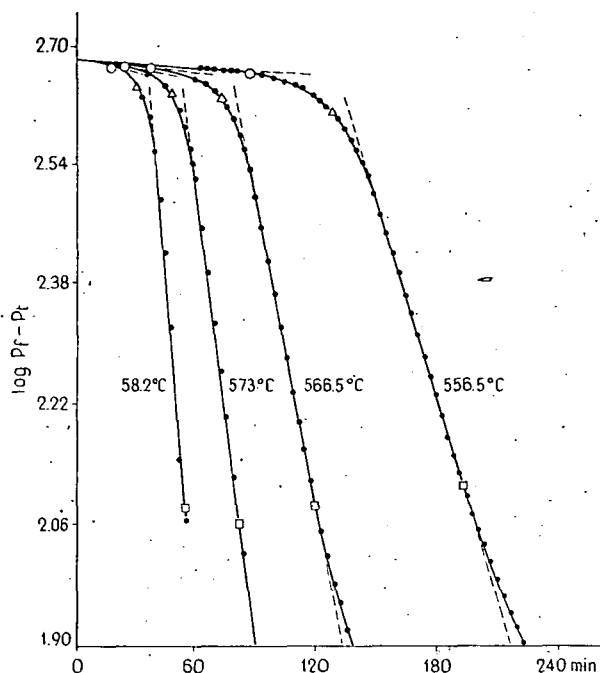

Fig. 16. Isothermal decomposition of $KClO_4$ at various temperatures: ● experimental points. Points calculated from phase diagram: o first phase change; △ end of melting; □ appearance of second solid phase [53]

The decomposition of potassium perchlorate in the solid phase was also studied by CORDES and SMITH [56]. The aim of their experiments was to investigate the solid-phase reaction under conditions where not even partial melting of the substance occurred. The extent of the decomposition in their experiments did not exceed 3.5%. The quantity of gases formed during the decomposition was measured with a Bendix "time of flight" mass-spectrometer, with the interesting result that on the initial heating of the substance to 400° C, not only oxygen but also CO_2, ClO_2 and Cl_2 were formed. If the potassium perchlorate was pre-treated overnight at 400—430° C, then chlorine dioxide and chlorine were no longer found and the amount of carbon dioxide was minimal, too. (It must be mentioned that the formation of foreign gases was earlier also observed in the decomposition of sodium azide

during mass-spectrometric analysis [57].) The compound could not be freed from the carbon dioxide impurity, even if the sample was previously treated with perchloric acid. The solid residue consisted of chlorate and chloride, in a ratio corresponding to the amount of oxygen evolved. The amount of the chlorate was about ten times that of the chloride. By converting the peak-height for the oxygen to the number of moles of oxygen evolved per second, the specific rate k_s was obtained. This rate value remained constant even after a long time, if the substance had been pretreated at 400° C in vacuum. In the log k_s vs. $1/T$ graph no hysteresis was obtained on the increase or decrease of the temperature. Arrhenius functions for different samples from the same substance were parallel straight lines in the temperature range studied. About 30—40° C below the melting point of the pure substance, however, the reaction rate suddenly increased and points taken at these temperatures did not lie on the Arrhenius functions. It was concluded from the constancy of the reaction rate that the growth of nuclei does not play an essential part in the reaction, which can thus be regarded as a homogeneous solid-phase decomposition.

In our view, one of the reasons for the absence of changes in reaction rate, characteristic of the formation and growth of nuclei, may be the 12-hour pre-treatment of the substance at a temperature (400—450° C) commensurable with the reaction temperature (350—450° C); during this period the above processes may have already taken place to a greater or smaller extent.

As regards the effect of the solid reaction product, it was found by GLASNER and WEIDENFELD [49] that even a small amount (mole ratio 0.1) of potassium chloride decreases the induction period of the decomposition, while a larger amount (mole ratio 1) eliminates it completely. The reaction rate constants and the activation energy are practically unaffected by the chloride.

Rubidium perchlorate

A kinetic study of the total decomposition of rubidium perchlorate was carried out at 547—569° C [35, 44]. The reaction began at once, without a time lag, and led to the formation of rubidium chloride. The α vs. t curves were sigmoid type. The reaction initially proceeded in the solid phase, but, similarly as for potassium perchlorate, with progressing decomposition the substance melted.

The decomposition in this case could be described by two first-order equations, the first of which referred to the slow solid-phase decomposition, and the second to the faster molten-phase decomposition. The activation energies were 70.5 and 66.8 kcal/mole, respectively. The decomposition was described surprisingly well by the PROUT—TOMPKINS relation which gave one straight line for practically the entire decomposition. The value of the activation energy was 71.3 kcal/mole. Here too, the addition of rubidium chloride to the rubidium perchlorate changed the decomposition to one of deceleratory nature and also significantly increased the rate of the decomposition.

Using the method reported above, CORDES and SMITH [56] also studied the decomposition of rubidium perchlorate in the solid phase. The characteristics of the reaction agreed with those for the potassium perchlorate reaction. The measured reaction rate was practically the same, but the value of the activation energy was somewhat lower.

F. SOLYMOSI

Table XI

Kinetic data of the decomposition of monovalent metal perchlorates

Compound	Temperature range °C	Method	Activation energy kcal/mole	Frequency factor (min⁻¹)	Kinetic equation	Validity of equation
$LiClO_4$	392—415	vacuum w-meas.	52.2	—	P—T	0.0 —0.4
		vacuum w-meas.	62.0		first order	0.4 —0.9
		vacuum w-meas.	58.3		time for decomp. of 0.5%	—
	411—431	vacuum p-meas.	52.6	$6,58 \cdot 10^{14}$	P—T	0.01—0.4
		vacuum p-meas.	41.0	$8.83 \cdot 10^{10}$	P—T	0,45—0.95
		vacuum p-meas.	43.9	$5.12 \cdot 10^{11}$	first order	0.4 —0.93
$NaClO_4$	330—420	chem. anal.	28.0	—	initial rate	—
	490—515	vacuum	57.3	$2.7 \cdot 10^{14}$	P—T	0.0—0.3
		p-meas.	57.1	$1.57 \cdot 10^{14}$	P—T	0.3—0.8
		p-meas.	59.2	$4.89 \cdot 10^{14}$	first order	0.55—0.95
		p-meas.	62.6	$1.8 \cdot 10^{15}$	CC	0.35—0.9
+ NaOH	360—420	in air,	47.3	$3.57 \cdot 10^{14}$	initial rate	ClO_4^- decomp.
		chem. anal.	53.2	$3.35 \cdot 10^{15}$	initial rate	ClO_3^- decomp.
$KClO_4$	536—617	in air, O_2, ml	60.6	—	first order	—
	537—600	in air, O_2, ml	65.8	$1.15 \cdot 10^{16}$	P—T	—
	556—582	vacuum	70.5	$1.42 \cdot 10^{15}$	first order	solid phase
		p-meas.	70.5	$7.86 \cdot 10^{16}$	first order	molten phase
	500—580	vacuum	98.4	$1.8 \cdot 10^{21}$	first order	solid phase
		p-meas.	80.7	$6.8 \cdot 10^{17}$	first order	molten phase
	375—480	chem. anal.	30.0	—	initial rate	—
	549—575	vacuum p-meas.	69.0	$1.16 \cdot 10^{15}$	first order	0.0 —0.15 (solid phase)
		p-meas.	71.5	$1.05 \cdot 10^{17}$	first order	0.3—0.9 (molten phase)
		p-meas.	75.4	$5.45 \cdot 10^{17}$	CC	0.28—0.85
	350—500	vacuum mas. spectr.	50.2	$3.78 \cdot 10^9$	initial rate	0.0 —0.03
	450—550	infra spectr.	44.3	—	second order	—
$RbClO_4$	547—569	vacuum	71.3	$1.03 \cdot 10^{17}$	P—T	0.3 —0.85
		p-meas.	70.4	$8.19 \cdot 10^{15}$	first order	0.01—0.28 (solid phase)

Table XI
(Continued)

Compound	Temperature range °C	Method	Activation energy kcal/mole	Frequency factor (min⁻¹)	Kinetic equation	Validity of equation
RbClO$_4$		p-meas.	66.8	$4.28 \cdot 10^{15}$	first order	0.4—0.92 (molten phase)
	350—500	p-meas.	72.3	$4.02 \cdot 10^{16}$	CC	0.2—0.95
		vacuum mass spectr.	46.0	$6.0 \cdot 10^{8}$	initial rate	0.0—0.03
CsClO$_4$	528—558	vacuum p-meas.	52.0	$2.68 \cdot 10^{12}$	P—T	0.1—0.7
		p-meas	68.7	$8.44 \cdot 10^{15}$	first order	0.01—0.25 (solid phase)
		p-meas.	57.0	$2.12 \cdot 10^{13}$	CC	0. —0.95
	385—475	chem. anal.	35.0	—	initial rate	—
	350—500	vacuum mass. spectr.	44.6	$1.90 \cdot 10^{8}$	initial rate	0.0—0.03
AgClO$_4$	414—445	vacuum p. meas.	62.7		P—T	0.01—0.33
			52.4		P—T	0.33—0.95
TlClO$_4$	409—452	vacuum p. meas.	56.0		P—T	

W-meas. = weight measurement
P-meas. = pressure measurement
P—T = Prout—Tompkins equation
CC = „Contracting cube" formula

Cesium perchlorate

The temperature of decomposition of cesium perchlorate is lower than that of rubidium perchlorate, and in fact, even lower than that of potassium perchlorate. Kinetic measurements were made at 528—558 °C by following the pressure of oxygen in vacuum [35]. The course of the reaction is similar to that observed for potassium and rubidium perchlorates. The rate maximum occurred at about $\alpha = 0.45$. Here too, the decomposition began in the solid phase, but as a result of the reaction product the substance melted below the melting point of the pure compound. The first-order equation gave a straight line for the initial solid-phase decomposition up to $\alpha = 0.23$. The value of the activation energy was 68.7 kcal/mole. The description of the liquid-phase decomposition with the first-order equation was much less successful. The PROUT—TOMPKINS relation gave one straight line for the total decomposition. The value of the activation energy was 52 kcal/mole. The values of the activation energies calculated from the temperature-dependence of the times for the various stages of the decomposition were in the range 67—70 kcal/mole. Here too, preliminary addition of the reaction product, cesium chloride, accelerated the decomposition to a considerable extent.

A significantly lower value of activation energy was obtained by CABANE and BENARD [45], and also by CORDES and SMITH [56]. The former authors carried out

their investigation at 385—475° C, the latter at 350—450° C, where the extent of the decomposition was less than 3—4%. The activation energy value obtained by CABANE and BENARD agreed well with that determined for the self-diffusion of ClO_4^- in cesium perchlorate.

The kinetic data referring to the thermal decomposition of the alkali metal perchlorates are given in Table XI.

Mechanism of decomposition of the alkali metal perchlorates

It is clear from the results of the kinetic studies that the decomposition of the alkali metal perchlorates is fairly complex, and several consecutive and simultaneous processes must be taken into consideration. In establishing the characteristics and the mechanisms of the decomposition, a difference must be made between the experiments extending to the total decompositions of the compounds at higher temperatures, and the studies concerned primarily with the surface reactions of the crystals. The evaluation of the results of the first experimental series is particularly difficult due to the phase-change during the reaction, and to the melting of the substances well below the melting points of the pure materials. Lithium perchlorate is an exception, the decomposition taking place completely in the liquid phase.

A general feature of the decompositions of alkali perchlorates is their auto-catalytic character. This is first of all the result of the melting of the compounds which is due to the effect of solid reaction products (chlorides). When the chlorides corresponding to the reaction products, were previously mixed to the perchlorate salts, the run of decompositions changed. The perchlorates melted at the very beginning of the decomposition, the autocatalytic character of the reaction disappeared and the decomposition started with a maximum rate. Accordingly, the catalytic effect of chlorides seems only apparent. The fact, however, that the decomposition of lithium perchlorate in the molten phase is also autocatalytic and the lithium chlorides exerted an accelerating effect on the decomposition, shows that the chloride might have some effect on the molten phase reaction in the former cases, too.

The values of activation energy of the decomposition of all alkali perchlorates were found to be in the range of 60—70 kcal/mole and practically the same for the solid and molten phase. This indicates that the chemical mechanism of the decomposition of perchlorates is essentially similar and the rate determining step, independently of the phases, is the same in every compound. The larger frequency factor obtained for decomposition in molten phase is probably the result of the larger mobility of the perchlorate ion. The decomposition of perchlorates can be thought as proceeding by the following steps. In the first step

$$MClO_4 \overset{k_1}{\rightleftharpoons} MClO_3 + \frac{1}{2} O_2 \qquad (40)$$
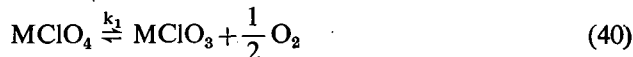
metal chlorate and oxygen are formed. The metal chlorate then decomposes partly into chloride and oxygen

$$MClO_3 \overset{k_2}{\rightleftharpoons} MCl + \frac{3}{2} O_2 \qquad (41)$$

and partly disproportionates into perchlorate and chloride

$$MClO_3 \overset{k_3}{\rightleftharpoons} \frac{3}{4} MClO_4 + \frac{1}{4} MCl. \qquad (42)$$
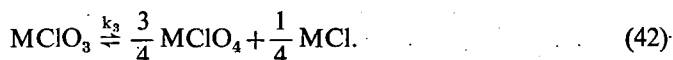
The occurrence of this latter reaction is indicated by experiments with chlorates. Although over 500° C the thermal decomposition of alkali chlorates is rapid, its disproportionation was observed even at this temperature. It is very likely that the decomposition of chlorate into chloride does not take place in one step but first chlorite is formed, which then decomposes into chloride

$$MClO_3 \overset{k_4}{\rightleftharpoons} MClO_2 + \frac{1}{2} O_2 \qquad (43)$$

$$MClO_2 \overset{k_5}{\rightleftharpoons} MCl + O_2. \qquad (44)$$
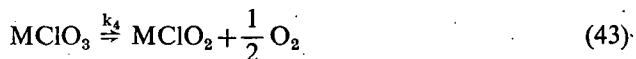
While the chlorate intermediate was found in decomposition of every alkali perchlorate, chlorite was not detected at all. The most plausible explanation for this seemed to be that at high temperature chlorites decompose extremely rapidly into chloride and oxygen. It was shown, however, that alkali chlorites did not decompose even in this temperature range into oxygen and chloride but instantaneously disproportionate into chlorate and chloride:

$$MClO_2 \overset{k_6}{\rightleftharpoons} \frac{2}{3} MClO_3 + \frac{1}{3} MCl. \qquad (45)$$
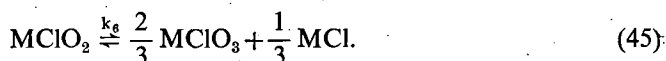
Regarding that alkali chlorates are less stable compounds than perchlorates $(k_2 > k_1)$ and their amount never exceeds 2—3 per cent during the reaction, it can be rightly assumed that in the decomposition of all alkali perchlorates the reaction (40) is the rate-determining step. This step involves the rupture of the Cl—O bond. The dissociation energy of the Cl—O bond (64.295 kcal/mole [15] is in good agreement with activation energies found experimentally.

A further proof for this mechanism can be obtained by calculating the endothermic heat of reaction of this step.

On the basis of the standard enthalpy of formation of perchlorates and chlorates, and supposing only a slight difference in their heat capacities, we obtain for ΔH^0 the value enlisted in the sixth column of Table XII. These values are much lower than the activation energies determined experimentally. Supposing, however, the formation of atomic oxygen ($\Delta H_f^0 = 59.2$ kcal) the data shown in the last column are obtained. These values, with the exception of that for lithium perchlorate, agree very well with the activation energies measured.

Besides the rupture of the Cl—O bond, one can suppose the electron-transfer reaction between the anion and the cation as the rate determining step of the decomposition:

$$M^+ + ClO_4^- = M + ClO_4. \qquad (46)$$

Table XII

Standard heat of formation for monovalent metal perchlorates and for their decomposition products

Compound	ΔH° MClO$_4$	ΔH° MClO$_3$	ΔH° MCl	ΔH° $\frac{1}{2}$M$_2$O	$\Delta H^{\circ}{}_{reac}.$	$\Delta H^{\circ}{}_{reac}.$
LiClO$_4$	−91.77	−70	−94.8	−71.3	21.77	80.9
NaClO$_4$	−92.18	−85.7	−98.23	−51.46	6.5	65.7
KClO$_4$	−103.6	−93.5	−104.17	−43.1	10.1	69.3
RbClO$_4$	−103.87	−93.8	−105.1	−41.5	10.0	69.2
CsClO$_4$	−105.86	−96.0	−106.4	−41.05	7.8	67.0
AgClO$_4$	−7.75	−5.73			2.02	61.2

The sixth and seventh columns contain the heat of reaction of the processes $MClO_4 = MClO_3 + \frac{1}{2} O_2$ and $MClO_4 = MClO_3 + O$, respectively.
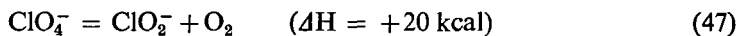
The electron-transfer reaction plays an important part in the decomposition of a number of ionic compounds as *e.g.* alkali azides. Of perchlorates, the decomposition of ammonium perchlorate between 200—300° C was supposed to take place according to this mechanism.

The thermal energy required for the transfer of an electron from the anion to the cation has been calculated from spectroscopic data in the case of potassium perchlorate [35]. The adsorption edge of alkali perchlorates is at about 6 eV [52], the low frequency dielectric constant (K) is 5.9 and the refractive index (n) is 1.4746. From these data the thermal activation energy was obtained to be 2.21 eV (51 kcal). Regarding that this value is much lower than the activation energy of the decomposition, we are of the opinion that the probability of an electron-transfer reaction can be excluded. The decomposition products (chloride and oxygen) are also against an electron-transfer reaction because in this case chlorine dioxide and chlorine must have been formed in the decomposition of the perchlorate radical or in the reaction between alkali metal and the perchlorate radical.
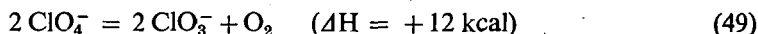
A separate discussion is required for the results of low temperature kinetic measurements when the decomposition occurred entirely on the surface layer of solid perchlorates and the conversion never exceeded 1—3%. The values of activation energies in one case [56] were between 40—50 kcal/mole and in another case [45] between 28—35 kcal/mole.

The values obtained by CABANE and BENARD [45] agreed with those measured in these compounds for the self-diffusion of the perchlorate ion; from this they concluded that the rate determining process of the thermal decomposition is the diffusion of the perchlorate ion.

Another explanation is offered by CORDES and SMITH [56] who considered two different modes of perchlorate decomposition; one of monomolecular type,

$$ClO_4^- = ClO_2^- + O_2 \qquad (\Delta H = +20 \text{ kcal}) \qquad (47)$$

$$ClO_2^- + ClO_4^- = 2 ClO_3^- \qquad (\Delta H = -7 \text{ kcal}) \qquad (48)$$

and one of bimolecular type,

$$2 ClO_4^- = 2 ClO_3^- + O_2 \qquad (\Delta H = +12 \text{ kcal}) \qquad (49)$$

The reaction heats of the above reaction steps, however, still differed from their experimentally determined activation energy values. If it is assumed that both starting steps lead to $^3\Sigma_g O_2$ and the multiplicity rules are valid for reactions occurring within a solid, the reported value of the reaction heat must be increased by at least 22 kcal/mole ($^1\Delta_g O_2$) assuming singlet ClO_4^- and ClO_3^-. The reaction heat values thus calculated are then consistent with the measured activation energy value.

It was attempted to decide between the two primary steps on the basis of the value of the frequency factor. The expected pre-exponential factor of the mono-molecular reaction step would be between 10^{11} and 10^{17} sec^{-1}, which is considerably higher than the experimentally determined value.

A bimolecular reaction could have such a low pre-exponential factor if the activated complex has restricted rotation while the reactants have free rotation. As activated complex, CORDES and SMITH suggested two adjacent ClO_4^- ions joined through a peroxide-like linkage, (O_3Cl)—O—O—(ClO_3). In the calculation of the rate constants by the activated complex theory the following assumptions were made;

— the external rotation are restricted to harmonic oscillations in the complex,
— the ClO_4^- ion is freely rotating,
— the torsion mode for the dihedral angle (ClO_3)—O—O—(ClO_3) is restricted by the lattice,
— the shortening of the Cl—Cl distance with respect to the value for the free ClO_4^- groups restricts the "pinwheel" rotations of the ClO_3 groups,
— the coulombic repulsion of the two charges affects only the activation energy and not the pre-exponential factor,
— the remaining internal vibrations are independent of the lattice forces,
— the transitional modes are represented by Einstein oscillators.

The force constant for the ClO_4^- ion was chosen to be the same as for KCl. The value obtained for the pre-exponential factor in the calculations, $1.2 \cdot 10^8$ sec^{-1}, was fairly close to the experimental value of 10^7 sec^{-1} and this was considered as a proof for the proposed mechanism. The change in Arrhenius factors with temperature was tentatively explained by the assumption that upon raising the temperature the lattice is able to open up to such an extent that the "pinwheel"-like motion of the ClO_3 groups is made possible, and, in addition, the other lattice constants also become weaker. The rate constant therefore increases, resulting in the increase of the value of the activation energy. This effect becomes even more pronounced when the substances melt.

Factors influencing the stability of alkali metal perchlorates

In spite of the fact that the temperature range of the decomposition of alkali metal perchlorates is relatively narrow, there are well defined differences between the temperatures of decomposition of these compounds. To characterize the stability of the substances, the temperature values have been calculated from the Arrhenius diagrams, where the rate constant of the decompositions (contracting cube formula) reaches the value of $5 \cdot 10^{-3}$. As it can be seen from Table XIII this characteristic temperature, increases from lithium to rubidium but it is lower for cesium.

As factors influencing the stability of perchlorates, the structural properties of the compounds, their physical constants and the character of the prevailing

Table XIII

Correlation between stability and bonding of metal perchlorates

Compound	Temp. of 2% decomp. °C [40]	T_0 (°C)	F*	Ionic character of M—ClO₄ bond %	Polarizing power of cations e/r	Polarisability of cations	Polarisability of oxygen ion in ClO_4^-
CsClO₄	601	526	1.303	75.5	0.592	3.34	26.1
RbClO₄	611	560	1.423	74.1	0.676	1.98	30.1
KClO₄	583	547	1.661	73.2	0.752	1.33	25.4
NaClO₄	522	508	2.407	68.9	1.053	0.41	25.3
LiClO₄	470	410	2.915	67.8	1.667	0.03	20.3

T_0 is the temperature value where the rate constant of the decompositions calculated by the contracting cube formula, $1-(1-\alpha)^{1/3}=kt$, reaches the value of $5 \cdot 10^{-3}$.

$F^* = \dfrac{Z^*}{r^2}$; where F* = effective electric field strength of cations

Z^* = effective nuclear charge

bonds have to be considered. Some of these properties are summarized in Table XIII. Evaluating the stability of perchlorates in the light of these data, it can be stated that *the more ionic a compound, the greater its stability*. The effective electric field strength of the cations affects the stability of perchlorates in a similar way. *The increase of the effective electric field strength of the cations results in a decrease of the temperature of the decomposition.* The only exception is cesium perchlorate, as its characteristic temperature is lower than that of the potassium salt. From among the physical properties of alkali metal perchlorates, the melting point of cesium prchlorate·shows a similar behaviour. Considering the fact, that the melting of inorganic compounds results in an enhanced rate of decomposition, it could be rightly assumed that the lower stability of cesium perchlorate is the consequence of its lower melting point.

In our opinion, however, the origin of the strange behaviour both in melting and stability of cesium perchlorate is to be found in the large size of the cesium ion and, consequently, in its more marked polarizability. This is reflected in the polarity of the Cl—O bond which is less in the case of cesium perchlorate than in rubidium perchlorate.

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КИНЕТИКА И МЕХАНИЗМ ТЕРМИЧЕСКОГО РАСПАДА ХЛОРИТОВ, ХЛОРАТОВ И ПЕРХЛОРАТОВ МЕТАЛЛОВ (ОБЗОР)

Ф. Шольмоши

Рассмотрены работы, занимающиеся вопросом термического распада хлоритов, хлоратов и перхлоратов разных металлов и дан критический обзор различных представлений о термических свойствах этих солей.