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DISPROPORTIONATION OF SOME ALKALI METAL CHLORITES IN THE SOLID PHASE

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Thermal behaviours of some alkali metal chlorites were studied under dynamic and isothermal conditions and some physical data of the chlorites were also determined. It was found that these chlorites disproportionate into chlorate and chloride in the solid phase without any measurable evolution of gas. The disproportionations were strongly exothermic. The values of the activation energies for the disproportionation reactions were found to be much smaller than the dissociation energy required for the rupture of the Cl–O bond. It was concluded that the disproportionations of alkali metal chlorites take place by rearrangement inside the lattice, without formation of atomic oxygen.

During the past twenty years there has been particularly great interest in the physical and chemical properties of the salts of halogen oxyacids [1]. The main reason for this is that many of these compounds are widely used in practice as a source of oxygen. They are employed in various pyrotechnic and explosive mixtures and also used in solid propellants.

As regards the salts of the oxyacids of chlorine, the physical and chemical properties of the perchlorates and the chlorates are the most well known. Fewer data are to be found on the chlorites, although, without a knowledge of the thermal behaviours of these salts, a reliable picture can not be obtained of the mechanisms of decomposition of the chlorates and perchlorates. The investigations to date indicate that chlorates can be demonstrated as intermediates in the decomposition of perchlorates, while chlorates are assumed to decompose via chlorites [1]. Chlorates and chlorites have the interesting property that their thermal decompositions are accompanied by parallel disproportionations in which an oxyanion of chlorine with a higher oxygen content is formed.

As a part of our research program for the better understanding of the thermal stabilities of chlorates and perchlorates, we undertook investigations of the thermal behaviours of different metal chlorites [2, 3]. We have now extended these investigations to some alkali metal, i.e. lithium, rubidium and caesium chlorites, the thermal behaviours of which are fundamentally different from those of the other metal chlorites. Besides kinetic investigations, we determined some important physical properties of the compounds relating to the type of bonding and the electronic structures of the substances.

Experimental

Materials

For the preparation of lithium, rubidium and caesium chlorites, the reaction:

$$M_2SO_4 + Ba(ClO_2)_2 = 2\,MClO_2 + BaSO_4$$

(M = Li, Rb, Cs) was used. 0.01 mole reagent grade alkali metal sulphate was dissolved in 5 ml distilled water, which was then added dropwise with constant stirring to 10 ml of solution containing 0.01 mole barium chlorite. The precipitated barium sulphate was filtered off and the solution was evaporated in vacuum up to crystallization. The chlorite salts were recrystallized twice and dried in vacuum. The products contained 99.5% chlorite. Samples were standardized by sieving, and sieve fractions with grain sizes of 80–100 μm were used. Barium chlorite was prepared by Levi's method [4].

Methods

For the thermal analysis of chlorites a Paulik–Paulik–Erdey type MOM derivatograph was used. The reference material was Al_2O_3. The disproportionation reaction under isothermal conditions was followed by chemical analysis. 50 mg samples were weighed into crucibles, which were then placed into an oven heated to the reaction temperature. After given periods the sample was dissolved in water. In the first test chlorite was determined by iodometric analysis in acetic acid solution. In the next aliquot the chlorite and chlorate contents were measured together, also by iodometric analysis, but in strong hydrochloric acid solution. In a new test the amount of chloride was measured by argentometric titration.

The refractive indices of metal chlorites were determined by the Becke line method using a Leitz microrefractometer. The low-frequency dielectric constant was measured in a Marconi RF 704 B instrument, using pellets 20 mm in diameter and 2 mm in thickness. Reflection spectra of the compounds were taken by a Unicam SP 500 instrument adapted for this purpose. Magnesium oxide served as reference material.

Results

Lithium chlorite

The TG, DTA and DTG curves of lithium chlorite are shown in Fig. 1. In the DTA curve the first exothermic peak is to be found at 215° and the second at 417°. Endothermic changes were observed at 70 and 593°. In the TG curve the weight loss began at 40° and continued up to 120°. This weight loss indicates the removal of adsorbed water. Similarly to the other alkali metal chlorites, lithium chlorite is extremely hygroscopic. It is important to mention that only a very small weight loss, of less than 1 %, was experienced during the first exothermic change. A large weight loss began at 342° and lasted up to 44°.

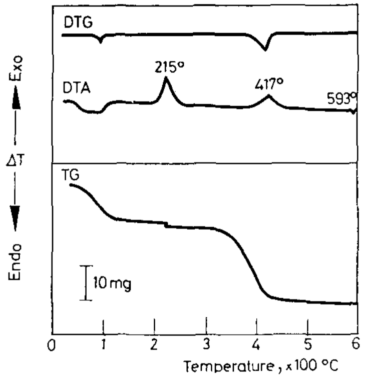

Fig. 1. TG, DTA, DTG curves of lithium chlorite; sample: 50 mg; heating rate: 3°/min

The measurement was interrupted at a number of temperatures, before and after the temperature of the first exothermic peak, and samples were subjected to thermal and chemical analysis. With interruption of the heating after the first exotherm, at 270°, and cooling of the sample down to room temperature, the substance did not exhibit the first exotherm in the repeated experiment. The material from the run interrupted at 170° still contained 58 % chlorite, whereas on interruption at 270° the chlorite content was less than 1 %. The residue consisted of a mixture of chlorate and chloride; its composition: 80.2 % lithium chlorate and 18.9 % lithium chloride. If the results of the thermal and chemical analytical studies are taken into account, it may be stated that, under the conditions of examination, lithium chlorite disproportionates with the liberation of heat (exotherm at 215°) but without gas evolution, in accordance with the following reaction:

$$3\,LiClO_2 = 2\,LiClO_3 + LiCl \qquad (1)$$

The weight loss beginning at 342° (in the TG curve) denotes decomposition of the chlorate. The latter is also an exothermic process, the peak temperature of which is to be seen at 417° in the DTA curve. The endothermic peak at 593° is indicative of the melting of lithium chloride.

Considering that a significant evolution of heat occurs in the solid above 200°, in the interest of ensuring isothermal conditions, the kinetic measurements were carried out in the range 150–180°. The percentage of lithium chlorate formed as a function of time at various temperatures is depicted in Fig. 2.

The reaction starts without an induction period, and the rate and extent of the transformation increase with the rise of the temperature.

The reaction was subjected to kinetic analysis with the first-order equation (Fig. 3). From the dependence of the logarithm of the rate constants as a function of reciprocal temperature, an activation energy of 24.2 kcal/mole was obtained (Table 1).

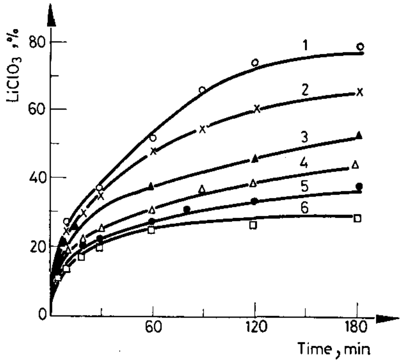

Fig. 2. Amount of lithium chlorate formed during the disproportionation of lithium chlorite. 1. 180°, 2. 176°, 3. 170°, 4. 165°, 5. 160°, 6. 152°

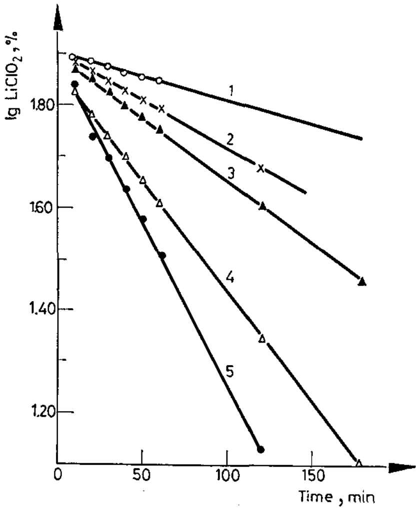

Fig. 3. Kinetic analysis of the disproportionation of lithium chlorite. 1. 152°, 2. 160°, 3. 165°, 4. 176°, 5. 180°

Table 1

Kinetic data of the disproportionations of alkali metal chlorites using the first-order equation

$LiClO_2$		$RbClO_2$		$CsClO_2$	
Temp. °C	$k_1 \cdot 10^{-4}$ min^{-1}	Temp. °C	$k_1 \cdot 10^{-4}$ min^{-1}	Temp. °C	$k_1 \cdot 10^{-4}$ min^{-1}
152	9.137	90	7.142	52	4.74
160	19.75	95	9.677	62	10.06
165	25.00	104	18.75	70	21.739
170	27.50	110	31.57	82	37.64
176	43.10	115	37.168	98	84.66
180	64.39	120	46.15		
Activation energy kcal/mole	24.21		19.29		15.20
Frequency factor, min^{-1}	$6.25 \cdot 10^8$		$2.86 \cdot 10^6$		$1.11 \cdot 10^5$

Rubidium chlorite

The TG, DTA and DTG curves of rubidium chlorite can be seen in Fig. 4. The first exothermic change to be found in the DTA curve begins at 134° and attains its maximum at 148°. From 28° up to 105° a weight loss of 13% was observed in the TG curve; this can be ascribed to loss of water. Here too the thermal analytical measurement was interrupted at several temperatures and chemical analysis was performed on the samples. The results demonstrated that rubidium chlorite undergoes complete disproportionation during the exothermic heat change. No decomposition (gas evolution) was observed here either.

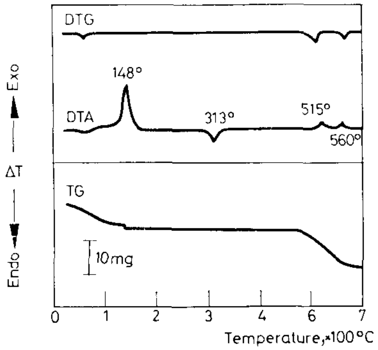

Fig. 4. TG, DTA, DTG curves of rubidium chlorite; sample: 50 mg; heating rate: 3°/min

The endothermic peak found at 313° in the DTA curve is a consequence of the melting of the rubidium chlorate formed. The subsequent exothermic changes can be ascribed to the decomposition of the chlorate and to that of the perchlorate formed by disproportionation of the chlorate. This is confirmed by the weight loss revealed in the TG curve.

The kinetic measurements were made at 90 – 120°, i.e. below the temperature of the beginning of the first exothermic peak to be found in the DTA curve. The amount of rubidium chlorate formed as a function of time at various temperatures is presented in Fig. 5. In this case too the first-order equation was suitable for a description of the reaction (Fig. 6). The activation energy was found to be 19.29 kcal/mole (Table 1).

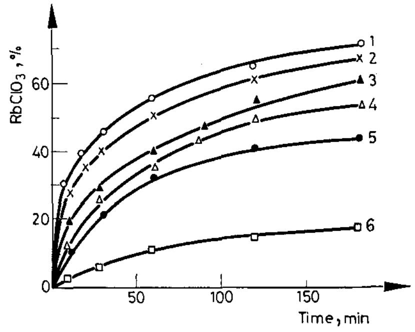

Fig. 5. Amount of rubidium chlorite formed during the disproportionation of rubidium chlorite. 1. 120°, 2. 115°, 3. 110°, 4. 104°, 5. 95°, 6. 90°

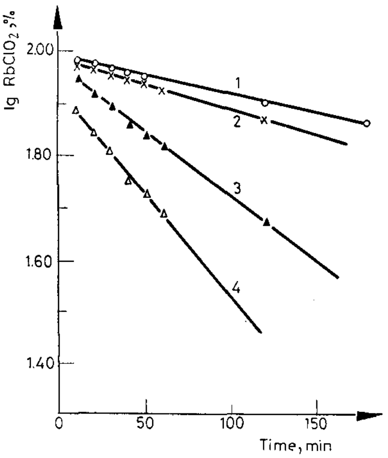

Fig. 6. Kinetic analysis of the disproportionation of rubidium chlorite. 1. 90°, 2. 95°, 3. 104°, 4. 115°

Caesium chlorite

Figure 7 shows the TG, DTA and DTG curves of caesium chlorite. The first exothermic change in the DTA curve begins at 110° and attains its maximum at 125°. The evolution of heat is again a consequence of the disproportionation of the chlorite. The weight loss from 30° denotes the desorption of adsorbed water.

Two endothermic peaks may be seen in the DTA curve. The first, at 298°, corresponds to a change in modification the caesium chlorate formed, and the second, at 335°, to the melting of the chlorate. The exothermic peak at 542° is an indication of the decomposition of the chlorate.

Kinetic measurements were carried out in the range 52–98°. Figure 8 shows the rate of formation of caesium chlorate at various temperatures. From the temperature-dependence of the rate constants calculated with the first-order rate equation, an activation energy of 15.20 kcal/mole was obtained. The kinetic data are listed in Table 1.

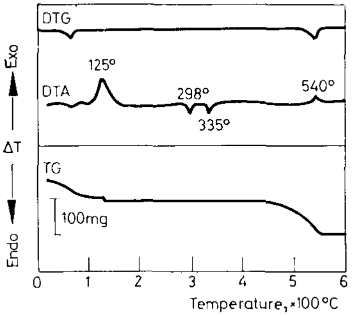

Fig. 7. TG, DTA, DTG curves of caesium chlorite; sample: 50 mg; heating rate: 3°/min

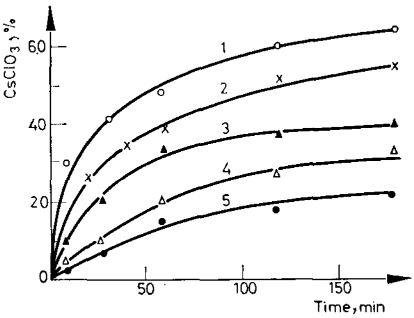

Fig. 8. Amount of caesium chlorite formed during the disproportionation of caesium chlorite. 1. 98°, 2. 82°, 3. 70°, 4. 62°, 5. 52°

Structures and some physical properties of the alkali metal chlorites

In the interest of establishing the factors affecting the thermal stabilities of the alkali metal chlorites and the possible mechanisms of their transformations, it is of importance that some physical properties, structures and bonding of the compounds be known.

Relatively few data are known on the physical properties of the chlorites. No data were found on even their melting points, which are of importance as regards the thermal stabilities of the compounds. Although the DTA curves presented above did not reveal endothermic changes indicative of melting of the substances, it can not be completely excluded that these remain hidden because of the heat evolution accompanying the disproportionations. In an attempt to solve this problem, alkali metal chlorite crystals were placed on a hot place of a microscope and the changes were observed when a heating rate of 5°/min was employed. It was found that potassium, rubidium and caesium chlorites do not melt in the temperature range of disproportionation. Melting was not observed either if the microscope slide was preheated to the temperature of disproportionation and the crystals were then placed onto it. The crystals melted only at the temperature of melting of the chlorate, indicating that chlorites disproportionated into chlorate during the heating. On the basis of this, it seems very likely that the partial melting exhibited during the heating of lithium chlorite at 190° for 18–20 min is also attributed to the melting of lithium chlorate (melting point: 129°) formed in the disproportionation reaction at 190°.

Some measurements were carried out with sodium chlorite, the disproportionation of which has been previously studied [2]. On a slide heated to 210° (the peak temperature of the exothermic change accompanying the disproportionation) sodium chlorite crystals did not vary until the 4th minute of observation, when they collapsed, with the sporadic formation of bubbles which burst. The bulk of the material melted, but the melt did also contain small solid particles too.

On the basis of the microscopic examinations, it may be stated that, with the exception of sodium chlorite, the alkali metal chlorites do not melt on being heated, but disproportionate before melting.

The reflection spectra of the alkali metal chlorites are presented in Fig. 9. They were very similar in character. The refractive index of each compound was also determined, and we obtained 1.545 for lithium chlorite, 1.525 for rubidium chlorite and 1.506 for caesium chlorite.

The low-frequency dielectric constants (K) were measured, and the high-frequency dielectric constants (K_0) were calculated in the knowledge of the refractive indices (n).

The quotient of the low-and high-frequency dielectric constants is much less than one for all the alkali metal chlorites, which points to the ionic nature of the compounds. This conclusion is supported by calculating the percentage ionic character of the bond according to Sanderson's method [5]. The ionic nature increases from lithium chlorite to caesium chlorite.

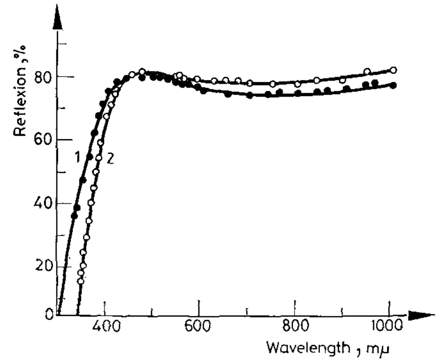

Fig. 9. Reflection spectra. 1. $RbClO_2$, 2. $CsClO_2$

The effective electric field strengths of the cations were calculated, too; these decrease from lithium ion to caesium ion. Data relating to the physical properties and bonding of the alkali metal chlorites are given in Table 2.

Table 2

Some physical constants of alkali metal chlorites*

Compound	Refractive index, n_D^{22}	$\frac{K_0}{K}$	Ionic radii according to Goldschmidt, Å	Polarizing power of cations, e/r	F^*	Ionic character of $M-ClO_2$ bond, %
$LiClO_2$	1.545	0.25	0.78	1.66	2.915	67.4
$NaClO_2$	1.501	0.34	0.98	1.05	2.407	68.3
$KClO_2$	1.483	0.53	1.33	0.75	1.661	73.0
$RbClO_2$	1.525	0.49	1.49	0.67	1.423	73.8
$CsClO_2$	1.506	0.31	1.65	0.59	1.303	75.1

$$F^* = \frac{Z^*e}{r^2} = \frac{(Z-S)e}{r^2}$$

F^* = effective electric field strength of cation,
Z^* = effective nuclear charge number, Z = nuclear charge,
S = screening number, r = radius of cation, $K_0 = n^2$

The percentage ionic character of the bond between the metal ion and the complex anion was calculated by Sanderson's method [5].

* This table contains the data of sodium and potassium chlorite [2, 6].

Discussion

Measurements showed that under both isothermal and dynamic conditions lithium, rubidium and caesium chlorites disproportionate into chlorate and chloride, practically without any measurable decomposition. This seems to be a general property of the alkali metal chlorites, as the same behaviour was experienced in the case of sodium [2] and potassium chlorite [6]. The less ionic chlorites (barium, silver and lead), however, behaved differently; at lower temperatures they disproportionated, but at higher temperature they exploded in very exothermic reactions [2]. Slow decomposition was observed only in the case of silver chlorite; the other compounds exploded immediately after commencement of gas evolution. Thallium(I) chlorite [7] displayed a fundamental difference from the above chlorites as regards its thermal behaviour: disproportionation was not observed at all and the compound exploded at room temperature as a result of even a mild mechanical action.

Before discussing the possible mechanisms ot the disproportionation of chlorites, it should be pointed out that thermodynamically it is possible that the chlorate is produced by the oxidation of chlorite with molecular oxygen (Table 3). Kinetically, however, in no case of chlorites was it observed.

Table 3

Heats of reaction of different transformations of sodium and potassium chlorite in kcal/mole, at 25 °

Compound	Heat of formation	ΔH_1	ΔH_2	ΔH_3	ΔH_4
$NaClO_2$	−72.65	−13.08	−17.24	−25.58	+22.95
$KClO_2$	−78.90	−14.60	−18.15	−25.27	+35.70

ΔH_1: for $MClO_2 + 1/2\ O_2 = MClO_3$
ΔH_2: for $MClO_2 = 2/3\ MClO_3 + 1/3\ MCl$
ΔH_3: for $MClO_2 = MCl + O_2$
ΔH_4: for $2\ MClO_2 = M_2O + Cl_2 + 3/2\ O_2$

Boyd and Brown [8] reported that, when solid potassium chlorite is heated and irradiated with γ-rays, chloride and chlorate anions are formed. They could not detect hypochlorite and perchlorate in the residue, and no oxygen was evolved during the disproportionation. Their results led them to assume that heat and irradiation produce oxygen atoms in the crystal lattice of the chlorite. The atomic oxygen reacts with remaining chlorite ions to yield chlorate:

$$ClO_2^- + O \rightarrow ClO_3^- \quad (2)$$

This conception resembles the assumption of Markowitz et al. [9] regarding the disproportionation of chlorates: they claimed that perchlorate is formed in a reaction between atomic oxygen produced in the decomposition of chlorate and undecomposed chlorate:

$$ClO_3^- + O \rightarrow ClO_4^- \quad (3)$$

If it were assumed that the alkali metal chlorites similarly undergo disproportionation with the participation of atomic oxygen, then the following reactions should be taken into account:

$$\mathrm{ClO_2^-} \xrightleftharpoons{w_1} \mathrm{ClO^-} + \mathrm{O} \tag{4}$$

$$\mathrm{ClO^-} \xrightleftharpoons{w_2} \mathrm{Cl^-} + \mathrm{O} \tag{5}$$

$$\mathrm{ClO_2^-} + \mathrm{O} \xrightleftharpoons{w_3} \mathrm{ClO_3^-} \tag{6}$$

$$\mathrm{ClO_2^-} + \mathrm{O} \xrightleftharpoons{w_4} \mathrm{ClO^-} + \mathrm{O_2} \tag{7}$$

$$s + \mathrm{O} + \mathrm{O} \xrightleftharpoons{w_5} \mathrm{O_2} + s \tag{8}$$

(s is the surface suitable for recombination of oxygen atoms).

The above reaction scheme shows that the formation of oxygen molecules is not appreciable only if the rate of recombination of oxygen atoms is substantially lower than the rate of the reaction between atomic oxygen and the chlorite ion and, in addition, if reaction (7) can be neglected. Accordingly, the following rate conditions hold: $w_5 \ll w_3$ and $w_4 \ll w_3$. Since the rates of all three reactions depend on the rate of formation of oxygen atoms, another condition for the absence of gas evolution is that $w_1 \ll w_3$, as otherwise the recombination of oxygen atoms will definitely occur.

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°, when the disproportionation reaction occurred instantaneously. Similar observations were made with the other alkali metal chlorites. If we accept the formation of, and oxidation by, atomic oxygen when chlorite is heated up to an elevated temperature, but still below the disproportionation temperature of chlorate, the oxygen atom should oxidize not only the remaining chlorite, but – to a smaller extent – the formed chlorate, too. From pure alkali metal chlorites, however, perchlorates did not form even at 200, 300, 350 and 400°. It is true that below 400° the transformation of alkali metal chlorates into perchlorates 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 chlorate.

The oxidation mechanism is also contradicted by the low activation energy values calculated from the kinetic measurements. According to the oxidation mechanism involving the participation of atomic oxygen, the slowest step of the process is reaction (4), i.e. the rupture of the Cl–O bond. In the event of this mechanism being the actual one, the activation energy of the reaction should approximate to the dissociation energy of the Cl–O bond, the calculated value of which is 64.295 kcal/mole [10]. We mention here that, in the decomposition of alkali metal chlorates and perchlorates where this step proved to be the rate-determining reaction, nearly the same values for activation energies were obtained [11, 12]. In the present case the activation energies of the reactions are substantially smaller (Table 1). In our view, the oxidation mechanism does not play an essential role in the disproportionations of the alkali metal chlorites; the disproportionations are rather the results of internal rearrangement processes between the chlorite ions. In this case, owing to the formation of the new Cl – O bond, evidently a lower energy input is required for the breaking of the original Cl – O bonds. The internal rearrangement is conceived in that, with the increase of temperature, simultaneously with the vibration and possibly rotation of the Cl – O bond, linkages are formed between the oxygens of the chlorites and the chlorines of the adjacent chlorites. Because of the thermodynamically higher stability of chlorate (which is the driving force of the transformation), this state is rearranged so that chlorate and chloride are formed. Our thermochemical calculations (Table 3) indicate that the internal rearrangements taking place in the crystal lattices of sodium and potassium chlorites are associated with the release of 13.25 and 18.15 kcal/mole reaction heat, respectively. It is probable that the situation is similar in the cases of the other alkali metal chlorites too, since the thermal analytical measurements proved the disproportionations to be exothermic processes. Unfortunately, the heats of formation of the other alkali metal chlorites are not yet known, and therefore the heats of reaction of the transformation of chlorites into chlorates can not be calculated in these cases.

Thermal analytic and kinetic measurements unambiguously show that the temperature of commencement of the disproportionation reaction decreases in the sequence:

$$LiClO_2, NaClO_2, KClO_2, RbClO_2, CsClO_2$$

The value of the activation energy slightly decreases in this order.

If the data in Table 2 (on the physical properties and bonding of these compounds and the characteristics of the cations) are taken into consideration, it may be stated that the smaller the effective field strength of the cation, and the larger the ionic nature of the compound, the lower the temperature at which the alkali metal chlorite disproportionates.

This correlation is exactly the opposite of that found between the thermal stabilities of the alkali metal perchlorates and chlorates, the properties of the cations and the ionic natures of the compounds [1]. With the increase of the effective electric field strength of the cation, the stabilities of these compounds decreased. A decreasing stability was also found with decrease of the ionic nature of the compound.

We consider that this opposite behaviour of the alkali metal chlorites supports our view that the disproportionations of the chlorites proceed by a fundamentally different mechanism from those of the decompositions of the chlorates and the perchlorates. It is highly probable that roles are played in the disproportionation order for the alkali metal chlorites by the crystal structures of the chlorites and also by the thermodynamic stabilities of the chlorates formed in the disproportionations of the chlorites.

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Résumé — Le comportement thermique de chlorites de métaux alcalins a été étudié en conditions de chauffage dynamique et isotherme. Quelques données physiques des chlorites ont aussi été déterminées. Il a été observé que ces chlorites se dismutent en phase solide en chlorate et chlorure sans dégagement mesurable de gaz. La dismutation est fortement exothermique. Les valeurs des énergies d'activation de la réaction de dismutation sont bien inférieures à l'énergie de dissociation nécessaire à la rupture de la liaison Cl—O. On en conclut que la dismutation des chlorites des métaux alcalins s'effectue par réarrangement à l'intérieur du réseau sans formation d'oxygène atomique.

Zusammenfassung — Das thermische Verhalten einiger Alkalimetallchlorite wurde unter dynamischen und isothermen Bedingungen untersucht und einige physikalischen Daten der Chlorite bestimmt. Es wurde festgestellt, daß diese Chlorite in fester Phase ohne meßbare Gasentwicklung zu Chloraten und Chloriden disproportionieren. Der Disproportionierungsvorgang war streng exotherm. Die für die Disproportionierungsreaktion festgestellten Werte der Aktivierungsenergie waren viel niedriger als die zur Spaltung der Bindung Cl—O benötigte Dissoziationsenergie. Es wurde gefolgert, daß die Disproportionierung von Alkalimetallchloriten durch Umordnung im Inneren des Gitters ohne Bildung von atomarem Sauerstoff erfolgt.

Резюме — Изучено термическое поведение некоторых хлоритов щелочных металлов в динамических и изотермических условиях и были определены некоторые физические данные этих хлоритов. Найдено, что исследованные хлориты диспропорционируют на хлораты и хлориды в твердой фазе без какого-либо выделяемого газа. Диспропорционирование является сильно экзотермичным процессом. Найдено, что значения активационных энергий реакции диспропорционирования намного меньше, чем энергия диссоциации, требуемая для разрыва связи Cl — O. Сделано заключение, что диспропорционирование хлоритов щелочных металлов происходит путем превращения внутренней решетки без образования атомного кислорода.