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# KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. XI THERMAL DECOMPOSITION OF SOME METAL DITHIONATES

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A thermal analytical study of Li, Na, K, Rb, Cs, $NH_4$, Mg, Ca, Sr, Ba and Zn dithionates is reported. The decomposition of the dithionate ion is endothermic in the case of the Na, K, Rb, Cs and $NH_4$ salts, but exothermic with Li, Mg, Sr, Ba and Zn. Kinetic parameters have been derived from the TG curves by means of the Coats-Redfern method. The validity of a linear kinetic compensation law is reported for the loss of crystal water and separately for the decomposition of the dithionate ion.

The thermal degradation of metal dithionates leads to the liberation of sulphur dioxide and to the formation of the corresponding sulphate. Under dynamic temperature conditions these processes have been studied by Torikai Eiichi et al. [1]. These authors established the decomposition schemes for several metal dithionates on the basis of TG, DTA and X-ray diffraction investigations. In our previous papers the thermal decomposition of metal dithionates was studied by means of derivatograph [2] and simple TG analysis [3]. In the last case an attempt was made to derive kinetic parameters by using Ozawa's method [4], but later this method was proved to be incorrect [5].

The kinetics of the thermal decomposition of Na and Ca dithionates were studied by Papazian et al. under dynamic temperature conditions [6]. Pavlyuchenko et al. [7] studied the kinetics of thermal decomposition of Ag, Mg, Ca, Sr and Ba dithionates under isothermal conditions and the catalytic effects of $Cd^{2+}$, $Ni^{2+}$, $Sr^{2+}$, $PbSO_4$ and $SnCl_2$.

In the present paper the thermal decompositions of $M(I)_2S_2O_6 \cdot xH_2O$ and $M(II)S_2O_6 \cdot xH_2O$ type compounds have been studied.

## Experimental

### *Method*

For the present thermal studies, a Derivatograph, described previously [8], was used. Generally 50 mg samples were used in conjunction with a platinum crucible and an air atmosphere.

*Preparation of the metal dithionates*

The starting material for the synthesis of these salts is $BaS_2O_6 \cdot 2H_2O$, which can be obtained from the reaction product of $MnO_2$ and $SO_2$ by treating with $Ba(OH)_2$ [9]. In order to obtain the other dithionates, the corresponding metal carbonates are dissolved in dithionic acid solution. 20 mmoles of $BaS_2O_6$ in 100 ml aqueous solution is passed through an ion-exchange column filled with Amberlit IR 120 cation exchanger in the R-H cycle. The effluent is treated with 20 mmoles of $MCO_3$ (or $M_2CO_3$). The dithionate solution is evaporated to effect crystallization.

The $NH_4$ salt is best prepared by the double decomposition reaction from $(NH_4)_2SO_4$ and $BaS_2O_6$ in stoichiometric ratio [10].

## Results and discussion

The substances studied are given in Table 1.

Table 1

Compositions of $M(I)_2S_2O_6 \cdot xH_2O$ and $M(II)S_2O_6 \cdot xH_2O$ studied

| M(I) | $x$ | M(II) | $x$ |
|---|---|---|---|
| $NH_4$ | 1 | Mg | 3 |
| | | Ca | 4 |
| Li | 2 | Sr | 4 |
| Na | 2 | Ba | 2 |
| K | 0 | Zn | 6 |
| Rb | 0 | | |
| Cs | 0 | | |

As seen from this Table, the salts of *K*, Rb and Cs, which have the largest ionic radii, do not contain crystallization water. In the case of these compounds the thermal decomposition corresponds to the single reaction:

$$M_2S_2O_6 = M_2SO_4 + SO_2 \quad (1)$$

In Fig. 1 typical thermal curves are given for these compounds.

The DTA curve shows a clear endothermic peak, corresponding to $SO_2$ evolution.

With all the other compounds studied, the first stage of thermal decomposition is the loss of the crystallization water. The salts of $NH_4$, Li, Na, Mg, Ca and Ba lose their crystallization water in a single step (Fig. 2). The Sr salt loses its crystallization water in two sucessive steps; in the first step 3 molecules of $H_2O$ are evolved and in the second step the fourth molecule (Fig. 3).

Special behaviour has been observed in the case of the Zn and $NH_4$ salts. Zn dithionate loses 5 molecules of water in the first stage; in the second stage

$SO_2$ is evolved and $ZnSO_4 \cdot H_2O$ is obtained. The last molecule of crystallization water is lost only above 200°. At about 700° the $ZnSO_4$ begins to lose $SO_3$ and at 900° it is transformed totally to ZnO. The $NH_4$ salt, after losing all its crystallization water, evolves $SO_2$ and $(NH_4)_2SO_4$ is obtained. The next stage is the loss of $NH_3$, and the $NH_4HSO_4$ obtained is completely volatilized between 350 and 420°.

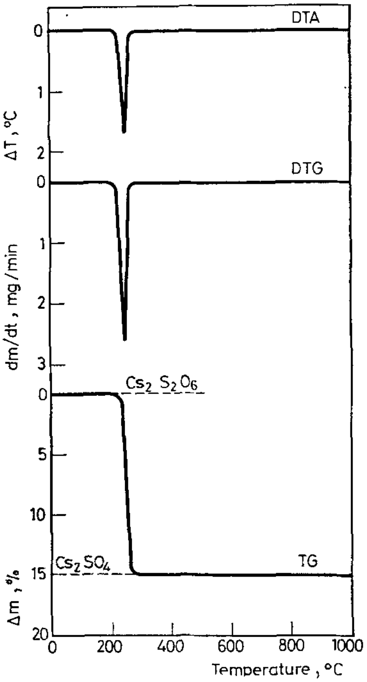

Fig. 1. DTA, DTG and TG curves of $Cs_2S_2O_6$

The other salts give sulphates, which remain unchanged up to 900°, only the Na and K salts are undergoing an endothermic phase transformation without weight loss, at about 850° (Fig. 4) and 580°, respectively.

As for as the thermal effect of reaction (1) or of the analogous reaction

$$MS_2O_6 = MSO_4 + SO_2 \qquad (2)$$

is concerned, this process is clearly endothermic in the case of the Na, K, Rb, Cs and $NH_4$ salts (see Figs 1 and 4), but exothermic for the other compounds studied (Li, Mg, Ca, Sr, Ba and Zn salts, see e.g. Figs 2 and 3).

By using the TG curves, a kinetic study has been made of the dehydration process and reactions (1) and (2). Coats and Redfern's [11] kinetic analysis method

Table 2

Kinetic parameters derived from the TG curves

| M | Loss of crystallization water | | | Reaction (1) or (2) | | | |
|---|---|---|---|---|---|---|---|
| | $n$ | $E_a$, kcal/mole | log $Z$ | $n$ | $E_a$, kcal/mole | log $Z$ | $t_{0.5}$, °C |
| Li | — | — | — | 1 | 63.4 | 24.9 | 243 |
| Na | 1 | 14.7 | 6.4 | 1 | 52.5 | 19.3 | 265 |
| K | — | — | — | 1 | 49.5 | 16.6 | 306 |
| Rb | — | — | — | 1 | 37.5 | 14.0 | 239 |
| Cs | — | — | — | 1 | 86.9 | 32.7 | 278 |
| $NH_4$ | 2/3 | 8.5 | 2.7 | 1 | 83.7 | 34.7 | 224 |
| Mg | 2/3 | 13.9 | 5.4 | 1 | 140.0 | 53.8 | 290 |
| Ca | 1 | 28.9 | 14.4 | 1 | 84.4 | 33.2 | 248 |
| Sr | 1 | 27.5 | 14.7 | 1 | 73.0 | 31.2 | 212 |
| Ba | 2/3 | 18.3 | 8.6 | 1 | 43.5 | 17.6 | 218 |
| Zn | 2/3 | 9.9 | 3.1 | 1 | 63.6 | 31.0 | 151 |

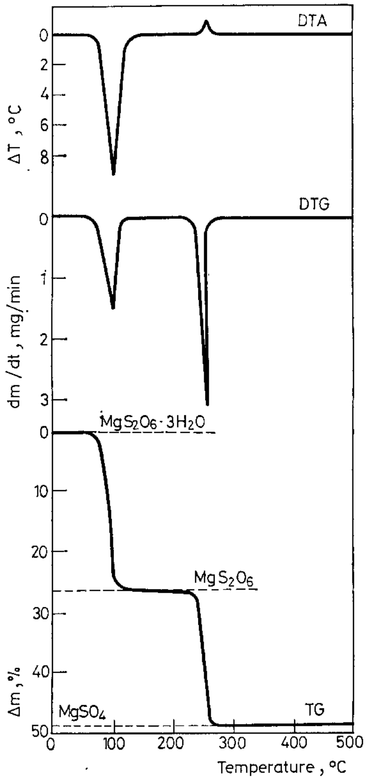

Fig. 2. DTA, DTG and TG curves of $MgS_2O_6 \cdot 3H_2O$

has been used. Apparent reaction order ($n$) and activation energy ($E_a$) values derived from our TG curves are presented in Table 2.

The same Table contains the log $Z$ values calculated by means of the formula [12]

$$\log Z = \log g(\alpha) - \log p(x) + \log R_q - \log E_a \tag{3}$$

where $Z$ is the formal Arrhenius preexponential factor expressed in $\sec^{-1}$, $g(\alpha)$ the conversion integral, $p(x)$ the exponential integral, $R$ the gas constant and $q$ the heating rate. The exponential integral values have been calculated by means of

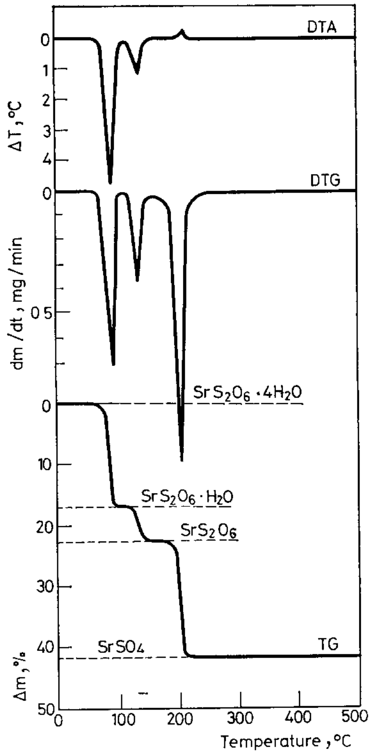

Fig. 3. DTA, DTG and TG curves of $SrS_2O_6 \cdot 4H_2O$

the appropriate approximation formula [13]. Conversion integrals $g(\alpha)$ have been calculated for different points of the TG curves by presuming apparent reaction orders $n = 0, 1/3, 1/2, 2/3$ and 1. Table 2 gives the $n$ values which ensured the linearity of the Coats-Redfern plot.

In the case of the decomposition of the dithionate ion, Table 2 also gives the temperatures $t_{0.5}$ at which the conversion reaches the value $\alpha = 0.5$. The thermal decomposition is seen to occur generally between 200 and 300°, with the exception of the Zn salt. It is easy to understand this exception, since $Zn^{2+}$ is the only cation

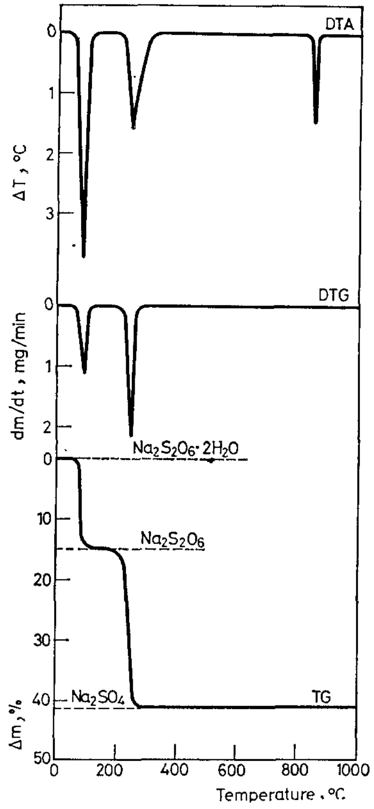

Fig. 4. DTA, DTG and TG curves of $Na_2S_2O_6 \cdot 2H_2O$

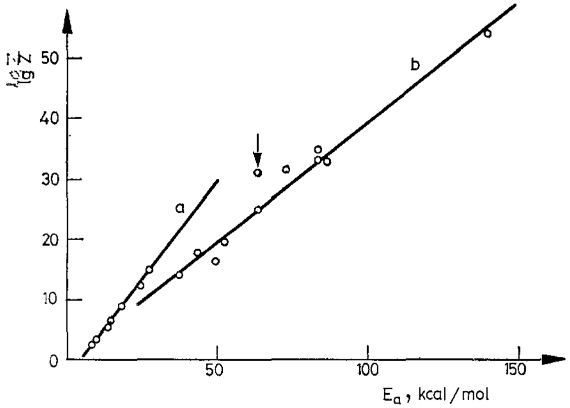

Fig. 5. The kinetic compensation effect; a, loss of crystallization water b, reactions (1) and (2)

having an $s^2p^6d^{10}$ external sphere electron configuration and consequently a large polarization effect facilitating the decomposition of the anion and leading to the decrease of the decomposition temperature. The other cations have a rare gas electron configuration.

Concerning the apparent activation energies of reactions (1) and (2), one can observe a decrease of $E_a$ with increasing ionic radius in the series Li – Na – K – Rb and Mg – Ca – Sr – Ba, but the $E_a$ value obtained for the Cs salt is in disagreement with the former regularity.

Conversely, one can observe the log $Z$ values to vary in parallel with the $E_a$ values, indicating a "kinetic compensation effect". The graphical plot of log $Z$ versus $E_a$ shows a good linearity both for the kinetic parameters obtained for the loss of crystallization water and also for the thermal decomposition of the dithionate ion, as seen from Fig. 5.

The only point situated far from the straight line is that of the Zn salt, indicated by an arrow in Fig. 5.

The compensation parameters $a$ and $b$ corresponding to the linear relation

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

have been calculated by using the least squares method. In these calculations the point corresponding to the Zn salt has been omitted. Results are presented in Table 3. In the last column of Table 3 Jaffé's correlation coefficient [14] is given. The values indicate good linearity.

Table 3

Compensation parameters

| Reaction | $a$ | $b$ | $r$ |
|---|---|---|---|
| Loss of crystallization water | 0.613 | −2.76 | 0.997 |
| (1) and (2)* | 0.395 | −0.45 | 0.991 |

* excepting the reaction of the Zn salt

As far as the slopes of the straight lines obtained are concerned, the $a$ value for the loss of crystallization water is practically the same as reported earlier [15] for analogous reactions. The $a$ value obtained for the decomposition of the $S_2O^{2-}$ ion is smaller than the values reported earlier [16 – 20] for different de-amination reactions of Co complexes, but larger than the $a$ value obtained for the decomposition of the $CO_3^{2-}$ ion in $CaCO_3$ [12], in good agreement with our hypothesis [15] concerning the correlation of the $a$ parameter with the bond strength between the leaving group and the part remaining in the solid phase.

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RÉSUMÉ — On présente les résultats d'une étude par analyse thermique des dithionates de Li, Na, K, Rb, Cs, $NH_4$, Mg, Ca, Sr, Ba et Zn. La décomposition est endothermique dans le cas des sels de Na, K, Rb, Cs et ammonium tandis qu'elle est exothermique dans le cas des sels de Li, Mg, Sr, Ba et Zn. Les paramètres cinétiques sont déduits des courbes TG par la méthode de Coats-Redfern. La validité d'une loi de compensation cinétique linéaire est étudiée pour la perte de l'eau d'hydratation ainsi que pour la décomposition de l'ion dithionate.

ZUSAMMENFASSUNG — Es wird über eine thermoanalytische Untersuchung der Dithionate von Li, Na, K, Rb, Cs, $NH_4$, Mg, Ca, Sr, Ba und Zn berichtet. Die Zersetzung des Dithionat-Ions ist im Falle von Na, K, Rb, Cs und $NH_4$-Salzen endotherm, im Falle von Li, Mg, Sr, Ba und Zn hingegen exotherm. Die kinetischen Parameter wurden aus den TG-Kurven mittels der Coats-Redfern-Methode abgeleitet. Es wird über die Gültigkeit eines linearen kinetischen Kompensationsgesetzes für den Verlust von Kristallwasser berichtet und gesondert für die Zersetzung des Dithionat-Ions.

Резюме — Приведено термическое аналитическое изучение дитионатов Li, Na, K, Rb, Cs, $NH_4$, Mg, Ca, Sr, Ba и Zn. Разложение дитионат иона в случае Na, K, Rb, Cs и $NH_4$ солей является эндотермическим, а в случае Li, Mg, Sr, Ba и Zn — экзотермическим. Кинетические параметры были выведены из кривых ТГ по методу Коутса—Рэдферна. Подтверждена справедливость линейно-кинетического компенсационного закона при потере кристаллизационной воды и отдельно при разложении дитионат иона.