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THERMAL STUDIES ON DITHIONATE COMPOUNDS. II. DITHIONATES OF LITHIUM, SODIUM, AND MAGNESIUM

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ABSTRACT

The decomposition of $Li_2S_2O_6 \cdot 2\,H_2O$, $Na_2S_2O_6 \cdot 2\,H_2O$, and $MgS_2O_6 \cdot 7\,H_2O$ has been studied using TG and DTG. Both sodium and lithium dithionates dehydrate in one step. Magnesium dithionate dehydrates in three separate steps. All three of the dithionates undergo further decomposition and lose sulfur dioxide to give stable sulfates. Kinetic parameters are presented for these reactions.

INTRODUCTION

Several thermal studies on dithionates have been reported [1–3]. Our previous studies on the decomposition of calcium, strontium, and barium dithionates have shown that they decompose to yield the corresponding sulfates by the loss of SO_2 [4]. Kinetic parameters were determined from the TG data. In general, it was found that for Group IIA metals as the size of the metal ion increases, the activation energy for loss of SO_2 decreases. In the present study, we have investigated the thermal decomposition of lithium, sodium, and magnesium dithionates.

EXPERIMENTAL

The $Li_2S_2O_6 \cdot 2\,H_2O$ was prepared by mixing solutions containing stoichiometric amounts of $BaS_2O_6 \cdot 2\,H_2O$ and Li_2SO_4, each dissolved in a minimum amount of water. The precipitate was separated by filtration. The solution containing $Li_2S_2O_6$ was concentrated to obtain the solid product which was then washed with ethyl alcohol followed by washing with absolute ether. The crystals were dried under vacuum. The $MgS_2O_6 \cdot 7\,H_2O$ was prepared in a similar manner using a solution of $MgSO_4$. The $Na_2S_2O_6 \cdot 2\,H_2O$ and $BaS_2O_6 \cdot 2\,H_2O$ were prepared as described by Pfanstiel [5].

TG studies were carried out using a Perkin-Elmer model TGS-2 thermo-

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gravimetric system. The procedures used were similar to those described previously [6]. Kinetic parameters were determined using the Coats and Redfern equations [7]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\frac{AR}{E\beta}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \qquad (1)$$

and for the case where $n = 1$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\frac{AR}{E\beta}\left(1-\frac{2RT}{E}\right)-\frac{E}{RT} \qquad (2)$$

where α is the fraction of the reaction completed, E is the activation energy, β is the heating rate, T is the temperature (K), A is the frequency factor, and R is the molar gas constant. The procedure of Reich and Stivala was also employed [8]. All calculations were done by computer using programs in FORTRAN.

RESULTS AND DISCUSSION

The TG and DTG curves for the decomposition of $Li_2S_2O_6 \cdot 2\,H_2O$, $Na_2S_2O_6 \cdot 2\,H_2O$, and $MgS_2O_6 \cdot 7\,H_2O$ are shown in Figs. 1, 2 and 3, respectively. From Figs. 1 and 2 it can be seen that both $Li_2S_2O_6 \cdot 2\,H_2O$ and $Na_2S_2O_6 \cdot 2\,H_2O$ dehydrate in a single step. After dehydration is complete, SO_2 is lost leaving the stable sulfate salts. Thus, the decomposition

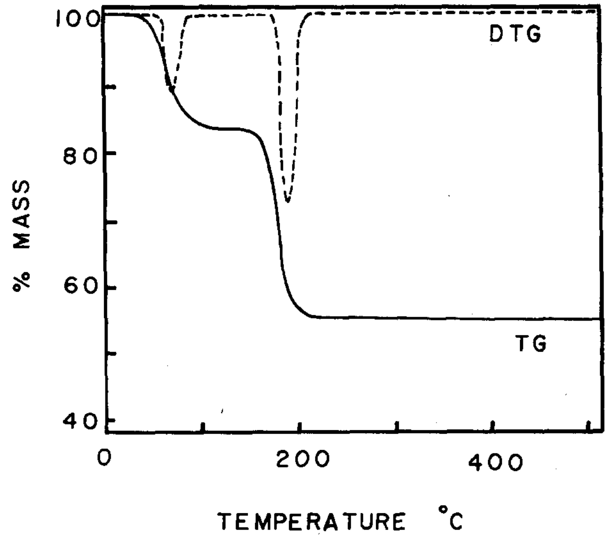

Fig. 1. TG and DTG curves for the decomposition of $Li_2S_2O_6 \cdot 2\,H_2O$.

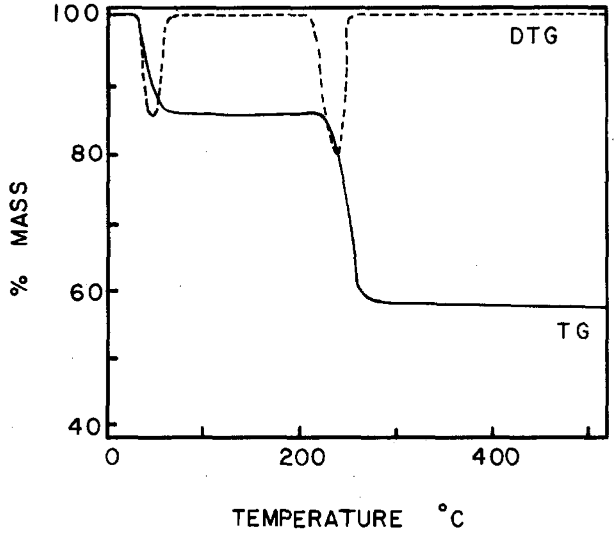

Fig. 2. TG and DTG curves for the decomposition of $Na_2S_2O_6 \cdot 2\ H_2O$.

reactions of these compounds are adequately represented by means of eqns. (3)–(6).

$$Li_2S_2O_6 \cdot 2\ H_2O(s) \rightarrow Li_2S_2O_6(s) + 2\ H_2O(g) \tag{3}$$

$$Li_2S_2O_6(s) \rightarrow Li_2SO_4(s) + SO_2(g) \tag{4}$$

$$Na_2S_2O_6 \cdot 2\ H_2O(s) \rightarrow Na_2S_2O_6(s) + 2\ H_2O(g) \tag{5}$$

$$Na_2S_2O_6(s) \rightarrow Na_2SO_4(s) + SO_2(g) \tag{6}$$

From Fig. 3 it can be seen that the dehydration of $MgS_2O_6 \cdot 7\ H_2O$ occurs

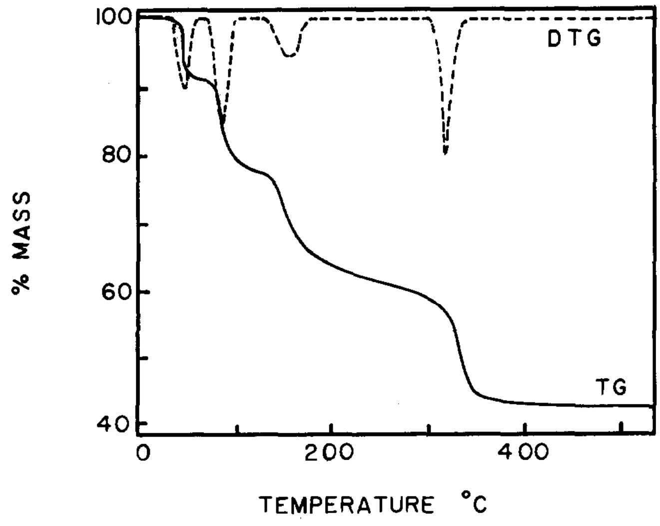

Fig. 3. TG and DTG curves for the decomposition of $MgS_2O_6 \cdot 7\ H_2O$.

in three separate steps. The first two steps consist of the loss of four water molecules with two molecules being lost in each step. In the third step, the remaining three molecules of water are lost. As in the previous cases, SO_2 is lost in the final transition. These reactions are shown in eqns. (7)–(10).

$$MgS_2O_6 \cdot 7\,H_2O(s) \rightarrow MgS_2O_6 \cdot 5\,H_2O(s) + 2\,H_2O(g) \tag{7}$$

$$MgS_2O_6 \cdot 5\,H_2O(s) \rightarrow MgS_2O_6 \cdot 3\,H_2O(s) + 2\,H_2O(g) \tag{8}$$

$$MgS_2O_6 \cdot 3\,H_2O(s) \rightarrow MgS_2O_6(s) + 3\,H_2O(g) \tag{9}$$

$$MgS_2O_6(s) \rightarrow MgSO_4(s) + SO_2(g) \tag{10}$$

The thermal parameters for the reactions shown in eqns. (3)–(10) are given in Table 1. The observed mass losses in each case were in good agreement with the theoretical values based on the equations.

There is no significant difference between the activation energies for the dehydration reactions except in the case of the intermediate $MgS_2O_6 \cdot 5\,H_2O$. In that case, the activation energy of 224 ± 32 kJ $mole^{-1}$ is significantly higher than the value of about 145 kJ $mole^{-1}$ exhibited by all the other dehydration reactions.

Previously we have reported the energies of activation for the loss of SO_2 from Ca, Sr, and Ba dithionates to be 301.4, 293.0, and 194.0 kJ $mole^{-1}$, respectively [4]. Thus, the activation energy of 275 ± 21 kJ $mole^{-1}$ for loss of SO_2 from MgS_2O_6 is very similar to the values obtained for dithionates of the other divalent metals, except barium. The strength of the S–S bond in the

TABLE 1

Reaction parameters for the decomposition of $Li_2S_2O_6 \cdot 2\,H_2O$, $Na_2S_2O_6 \cdot 2\,H_2O$, and $MgS_2O_6 \cdot 7\,H_2O$

Equation	Temp. range (K)	% Mass loss		Reaction order [a]		E_a (kJ $mole^{-1}$) [a]	
		Calcd.	Obsd.	R–S [b]	C–R [c]	R–S [b]	C—R [c]
$Li_2S_2O_6 \cdot 2\,H_2O$							
(3)	327–347	17.2	15.8	1.3	1.3	144 ± 9	145 ± 4
(4)	455–479	30.5	29.4	1.2	1.2	383 ± 14	381 ± 5
$Na_2S_2O_6 \cdot 2\,H_2O$							
(5)	305–331	14.9	14.3	1.5	1.4	152 ± 13	146 ± 4
(6)	513–530	26.5	26.7	1.2	1.0	366 ± 13	334 ± 13
$MgS_2O_6 \cdot 7\,H_2O$							
(7)	307–327	11.6	10.5	1.2	1.2	148 ± 6	141 ± 11
(8)	347–379	11.6	12.6	1.3	1.4	217 ± 21	224 ± 32
(9)	407–491	17.4	16.0	2.4	2.7	132 ± 9	147 ± 11
(10)	575–619	20.6	18.7	0.4	0.3	273 ± 23	275 ± 21

[a] Shown as average values for several determinations.

[b] Reich and Stivala method [8].

[c] Coats and Redfern method [7]. Increments of 0.333... used for *n* determination.

H_2S_2 molecule has been given as 268 ± 21 kJ mole^{-1} while that in the S_8 molecule is 226 kJ mole^{-1} [9]. If the S–S bond energy in $S_2O_6^{2-}$ is similar to that in H_2S_2, it appears that the loss of SO_2 from all of the dithionates of divalent metals requires an activation energy that is about equal to the strength of the S–S bond that must be broken. It would appear that somewhat higher activation energies would be required if breaking the S–S bond also resulted in some lattice expansion against the lattice energy. While the differences are slight, it appears that in each case, except BaS_2O_6, the activation energies are at least as great or slightly greater than the S–S bond energy. The barium compound is initially a dihydrate while the magnesium, calcium, and strontium compounds have higher numbers of hydrate water. It may be that loss of more water in the latter cases causes extensive changes that result in a more difficult loss of SO_2 from these compounds. The order of reaction for loss of SO_2 from BaS_2O_6 is also different [4]. The activation energies are thus seen to decrease slightly with an increasing size of the metal ion, but the differences are probably not outside the range of experimental error. This would be expected on the basis of a decrease in lattice energy as the size of the cation increases.

It is surprising that the activation energies are of comparable magnitude of the S–S bond energy since other changes are also necessary for SO_2 to be liberated. For example, an S–O bond must also be broken. It may be that the orientation of the $S_2O_6^{2-}$ ion in the crystal is such that removal of an oxygen atom is facilitated by the presence of cations of high charge density. At any rate, the activation energy for loss of SO_2 is remarkably independent of the nature of the divalent metal ion present except in the case of Ba^{2+}. We have no ready explanation of the unusually low activation energy in that case.

The loss of SO_2 from either $Li_2S_2O_6$ or $Na_2S_2O_6$ has a higher activation energy than that for the divalent metal dithionates. Because there are two cations per anion in these compounds, a greater degree of lattice deformation can be expected as SO_2 escapes. Accordingly, the univalent dithionates have higher activation energies for loss of SO_2.

REFERENCES

1 G. Tammann and W. Boehone, Z. Anorg. Chem., 203 (1932) 143.
2 H.A. Papazian, P.J. Pizzolato and J. Peng, Thermochim. Acta, 5 (1972) 147.
3 P.K. Gallagher, S.S. Abrahams and R. Limiaga, Thermochim. Acta, 41 (1980) 291.
4 G.L. Jeyaraj and J.E. House, Jr., Thermochim. Acta, 66 (1983) 289.
5 R. Pfanstiel, Inorg. Synth., 2 (1946) 167.
6 J.E. House, Jr., G.L. Jepsen and J.C. Bailar, Jr., Inorg. Chem., 18 (1979) 1397.
7 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
8 L. Reich and S.S. Stivala, Thermochim. Acta, 36 (1980) 103.
9 J.E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, Harper and Row, New York, 2nd edn., 1978, p. 849.