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THERMAL STUDIES ON DITHIONATE COMPOUNDS.
III. Dithionates of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II)

J. E. House, Jr. and *G. L. Jeyaraj*

DEPARTMENT OF CHEMISTRY, ILLINOIS STATE UNIVERSITY,
NORMAL, ILLINOIS 61761, U.S.A.

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TG and DTG studies have been carried out on $CoS_2O_6 \cdot 6\,H_2O$, $NiS_2O_6 \cdot 6\,H_2O$, $CuS_2O_6 \cdot 3.5\,H_2O$, $ZnS_2O_6 \cdot 6\,H_2O$ and $CdS_2O_6 \cdot 4\,H_2O$. After partial dehydration, the dithionates of Co(II), Ni(II), Cu(II) and Zn(II) lose water and sulfur dioxide simultaneously to yield the stable metal sulfates in the final step of decomposition. The $CdS_2O_6 \cdot 4\,H_2O$ dehydrates completely in the first two steps of decomposition with two water molecules being lost in each step. In the third step, it loses only SO_2 to yield $CdSO_4$. Kinetic parameters are presented for these reactions.

Several metal dithionates have been studied by many workers in the recent past using thermal methods of analysis [1, 2]. In our previous studies on the Group-IA and Group-IIA metal dithionates, we reported that in all cases complete dehydration of the compounds takes place in single or multiple steps prior to the loss of sulfur dioxide to yield a stable metal sulfate [3, 4]. In the present work, our studies on dithionates have been extended to investigate the thermal behavior of dithionates of Co(II), Ni(II), Zn(II) and Cd(II).

Experimental

The metal dithionates used in this work, $CoS_2O_6 \cdot 6\,H_2O$, $NiS_2O_6 \cdot 6\,H_2O$, $CuS_2O_6 \cdot 3.5\,H_2O$, $ZnS_2O_6 \cdot 6\,H_2O$ and $CdS_2O_6 \cdot 4\,H_2O$, were prepared by mixing aqueous solutions containing stoichiometric amounts of the corresponding metal sulfate and $BaS_2O_6 \cdot 2\,H_2O$. The white precipitate of $BaSO_4$ was removed by filtration and the solution containing the metal dithionate was evaporated to a small volume and then cooled to crystallize the metal dithionate. In each case, the crystalline product was filtered, washed with ethanol and ether and dried under vacuum. The $BaS_2O_6 \cdot 2\,H_2O$ was prepared using the method described by Pfanstiel [5].

TG studies were carried out in a nitrogen atmosphere using a Perkin–Elmer model TGS-2 thermogravimetric system. The procedures used were similar to those described previously [6]. Infrared spectral studies were performed on a Perkin–Elmer model 621 Grating Spectrometer.

Both the Coats and Redfern equations [7] and the Reich and Stivala method [8] were employed for the determination of kinetic parameters from the TG data. The equations used in the analysis by the Coats and Redfern method were,

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

and for the case where $n = 1$,

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

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. Calculations were carried out by computer using FORTRAN programs.

Results and discussion

Figures 1–5 show the TG and DTG curves for $CoS_2O_6 \cdot 6\,H_2O$, $NiS_2O_6 \cdot 6\,H_2O$, $CuS_2O_6 \cdot 3.5\,H_2O$, $ZnS_2O_6 \cdot 6\,H_2O$ and $CdS_2O_6 \cdot 4\,H_2O$, respectively, The TG curves show that with the exception of $CuS_2O_6 \cdot 3.5\,H_2O$, the decomposition of the above dithionates takes place in three distinct steps. However, the analysis of percentage mass loss indicates that the decomposition reactions of $CdS_2O_6 \cdot 4\,H_2O$ are different from those of $CoS_2O_6 \cdot 6\,H_2O$, $NiS_2O_6 \cdot 6\,H_2O$ and $ZnS_2O_6 \cdot 6\,H_2O$, and this difference is apparently due to the stability of the various intermediate aquo complexes. The decomposition reactions for the dithionates of cobalt, nickel and zinc can be represented by equations (3)–(6) where $M = Co^{2+}$, Ni^{2+} or Zn^{2+}.

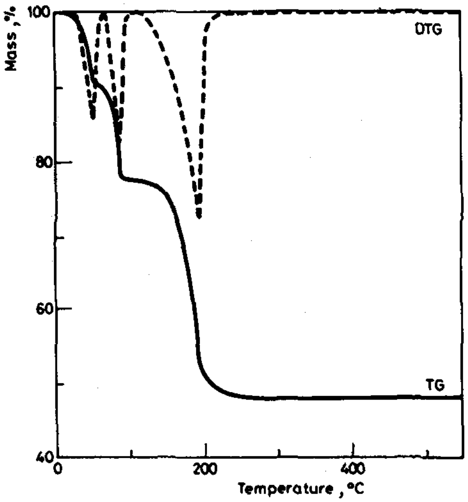

Fig. 1 TG and DTG curves for the decomposition of $CoS_2O_6 \cdot 6\,H_2O$ in N_2 at 10° min^{-1}

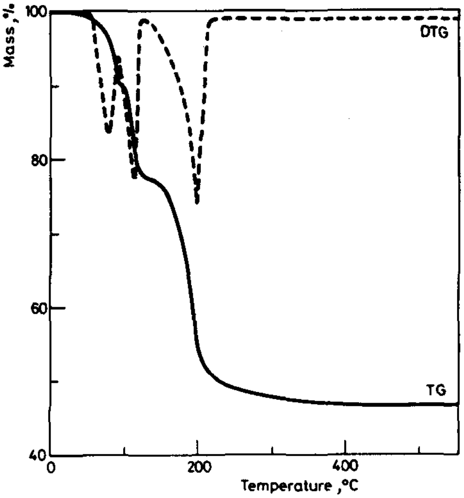

Fig. 2 TG and DTG curves for the decomposition of $NiS_2O_6 \cdot 6\ H_2O$ in N_2 at 10° min^{-1}

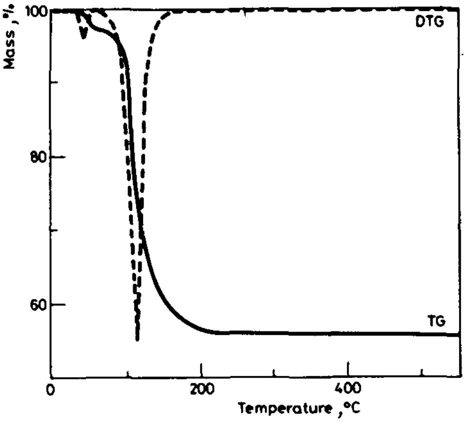

Fig. 3 TG and DTG curves for the decomposition of $CuS_2O_6 \cdot 3.5\ H_2O$ in N_2 at 10° min^{-1}

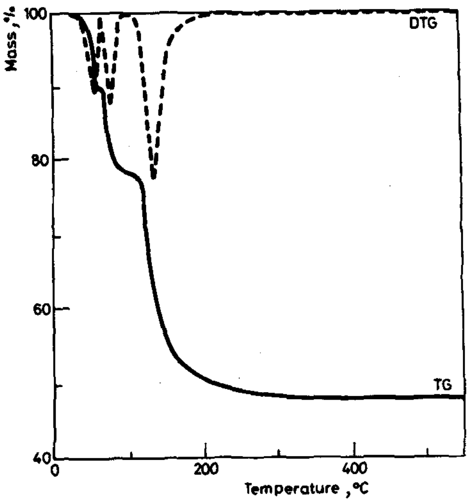

Fig. 4 TG and DTG curves for the decomposition of $ZnS_2O_6 \cdot 6\,H_2O$ in N_2 at 10° min^{-1}

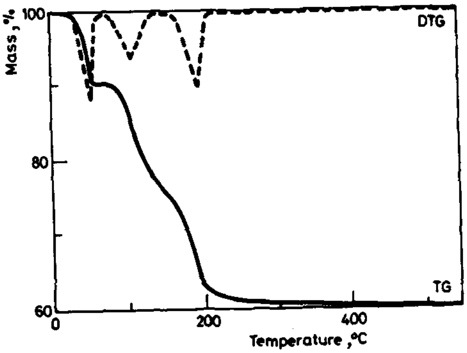

Fig. 5 TG and DTG curves for the decomposition of $CdS_2O_6 \cdot 4\,H_2O$ in N_2 at 10° min^{-1}

$$MS_2O_6 \cdot 6\,H_2O(s) \longrightarrow MS_2O_6 \cdot 4\,H_2O(s) + 2\,H_2O(g) \quad (3)$$

$$MS_2O_6 \cdot 4\,H_2O(s) \longrightarrow MS_2O_6 \cdot 2\,H_2O(s) + 2\,H_2O(g) \quad (4)$$

$$MS_2O_6 \cdot 2\,H_2O(s) \longrightarrow MSO_4(s) + SO_2(g) + 2\,H_2O(g) \quad (5)$$

The decomposition reactions of copper and cadmium compounds are shown in Eqns (6)–(10).

$$CuS_2O_6 \cdot 3.5\ H_2O(s) \longrightarrow CuS_2O_6 \cdot 3\ H_2O(s) + \frac{1}{2} H_2O(g) \quad (6)$$

$$CuS_2O_6 \cdot 3\ H_2O(s) \longrightarrow CuSO_4(s) + SO_2(g) + 3\ H_2O(g) \quad (7)$$

$$CdS_2O_6 \cdot 4\ H_2O(s) \longrightarrow CdS_2O_6 \cdot 2\ H_2O(s) + 2\ H_2O \quad (8)$$

$$CdS_2O_6 \cdot 2\ H_2O(s) \longrightarrow CdS_2O_6(s) + 2\ H_2O \quad (9)$$

$$CdS_2O_6(s) \longrightarrow CdSO_4(s) + SO_2(g) \quad (10)$$

From equations (3)–(10), it can be seen that in the first two decomposition steps of all dithionates except $CuS_2O_6 \cdot 3.5\ H_2O$, two water molecules are lost per step. In the case of $CoS_2O_6 \cdot 6\ H_2O$, $NiS_2O_6 \cdot 6\ H_2O$ and $ZnS_2O_6 \cdot 6\ H_2O$, two water molecules and sulfur dioxide are lost simultaneously in the third step of decomposition (while $CuS_2O_6 \cdot 3.5\ H_2O$ loses three molecules of water together with SO_2 in the second and final step). But $CdS_2O_6 \cdot 4\ H_2O$ loses all four water molecules in the first two steps of decomposition and only sulfur dioxide in the final decomposition step.

To confirm the simultaneous loss of SO_2 and H_2O in the third step of decomposition of the dithionates of Co, Ni, Cu and Zn, intermediate products were isolated and analysed using infrared spectroscopy. The hexahydrates and the products after the first and second decomposition step showed a broad band in the region of 3600–3100 cm^{-1} while the final product did not show any absorption in that region. The absorption band in the region of 3600–3100 cm^{-1} is due to the O–H stretching of the water molecules and it is broad due to hydrogen bonding, probably with the oxygen of the $S_2O_6^{2-}$ group. This information confirmed that the loss of SO_2 and H_2O takes place simultaneously in the third decomposition step of the dithionates of Co, Ni, Cu and Zn.

The linear regression analysis of the data obtained from several samples was carried out using the Coats and Redfern method [Eqns (1) & (2)] and the Reich and Stivala method. The thermal parameters for the decomposition of the dithionates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are shown in Table 1. It can be seen from the table that the values obtained for the energy of activation and order of reaction using the above mentioned methods are in good agreement except for the cases where the order of reaction was zero.

For all the dithionates except $CuS_2O_6 \cdot 3.5\ H_2O$, the first step of the dehydration reaction was found to be a first order reaction and the activation energies were in the range of 108 to 142 kJ $mole^{-1}$. The $CuS_2O_6 \cdot 3.5\ H_2O$ loses 0.5 molecule of H_2O in the first step of decomposition and the order of reaction was 2.3 with an activation energy of 201 ±36 kJ $mole^{-1}$ being indicated.

Unlike the first step of decomposition, in the second step only the dithionates of Co(II), Ni(II) and Zn(II) gave the same value for the order of reaction and it was equal to 4/3. For $CdS_2O_6 \cdot 4\ H_2O$, the order of reaction for the second step of decomposition was one. In the second step of decomposition, the copper dithionate loses its remaining three water molecules together with sulfur dioxide to yield the stable anhydrous $CuSO_4$. The order of reaction for this process was 2 with an activation energy of 162±2 kJ mole^{-1}.

The loss of H_2O from $CdS_2O_6 \cdot 4\,H_2O$ has a significantly lower activation energy than for the loss of water from the corresponding Co(II), Ni(II) and Zn(II) compounds. This is not unexpected considering that Cd(II) is a second transition series metal ion and is, therefore, a softer electron pair acceptor than the first series metal ions of the same charge. With H_2O being a hard Lewis base, the aquo complexes of Cd(II) are less stable than those of Co(II), Ni(II) and Zn(II). The lower stability of the aquo complexes of Cd(II) apparently results in the original complex being obtained as the tetrahydrate rather than the hexahydrate.

In the dithionates of cobalt(II) and nickel(II), the loss of H_2O and SO_2 takes place in the third and final step of decomposition and the temperature ranges are almost the same (between 115 and 225°). The same process in $ZnS_2O_6 \cdot 6\,H_2O$ begins near 105° and is completed near 162°. The $CdS_2O_6 \cdot 4\,H_2O$ behaves in a different way from the other dithionates and loses only SO_2 in the third step to give the stable $CdSO_4$.

The results in Table 1 show that the pattern of thermal behavior is the same for the dithionates of first series of transition metals studied in this work, except for copper. The anomalous behavior of copper complexes has also been observed in other compounds such as $CuSO_4 \cdot 5\,H_2O$. Although the dithionates of Co(II), Ni(II), Zn(II) have the same pattern of thermal decomposition and same reaction orders for the first two steps of decomposition, the results show that the zinc dithionate does not follow the same rate law that is followed by the dithionates of Co(II) and Ni(II). The analysis of the data obtained for the loss of SO_2 and H_2O in the final step of decomposition of the zinc dithionate using the Coats and Redfern method gave results contrary to those obtained by the Reich and Stivala method. The results obtained by the former method showed the order of reaction was greater than 50 with an activation energy in the order of 10.000 kJ mole^{-1}. This is based on the fact that the correlation coefficient was still increasing as n reach a value of 50. The Reich and Stivala method showed that the same process was a zero order reaction with an activation energy greater than 1000 kJ mole^{-1}. However, the intercept was much too high since the correct value of n should result in an intercept of zero. These are the results which indicated that zinc dithionate does not follow the rate law used in Coats and Redfern analysis. This situation precludes determining reliable kinetic parameters for this reaction given in Eq. (5) where $M = Zn$.

The energies of activation for the third decomposition step of $CoS_2O_6 \cdot 6\,H_2O$ and $NiS_2O_6 \cdot 6\,H_2O$ were 76±2 and 64±3 kJ mole^{-1}, respectively. These values for reactions that involve simultaneous loss of H_2O and SO_2 are much lower than the 250–300 kJ mole^{-1} observed for loss of SO_2 alone from Group-IA and Group-IIA dithionates [3, 4]. In the case of the alkali and alkaline earth dithionates, the loss of SO_2 must involve breaking the S–S bond (about 268 kJ mole^{-1}) and expanding the lattice to allow SO_2 to diffuse out of the crystal [9]. In the case of the transition metal compounds, it is quite likely that coordinated H_2O molecules can interact

Table 1 Thermal parameters for the decomposition of $CoS_2O_6 \cdot 6\,H_2O$, $NiS_2O_6 \cdot 6\,H_2O$, $CuS_2O_6 \cdot 3.5\,H_2O$, $ZnS_2O_6 \cdot 6\,H_2O$ and $CdS_2O_6 \cdot 4\,H_2O$

Equations	Temp. range, °C	% Mass loss		Reaction order+		E_a, kJ mole^{-1} +	
		Calcd.	Obsd.	R–S[a]	C–R[b]	R–S[a]	C–R[b]
$CoS_2O_6 \cdot 6\,H_2O$							
(3)	56–85	11.0	10.9	1.0±0.10	1	146±12	142±14
(4)	86–112	11.0	11.4	1.4±0.07	4/3	270±10	260±8
(5)	121–225	30.6	31.0	0.0±0.00	0	–*	64±3
$NiS_2O_6 \cdot 6\,H_2O$							
(3)	30–65	11.0	11.0	0.9±0.22	1	108±17	108±10
(4)	66–107	11.0	11.1	1.5±0.19	4/3	194±6	185±11
(5)	115–220	30.6	30.1	0.0±0.00	0	–*	76±2
$CuS_2O_6 \cdot 3.5\,H_2O$							
(6)	35–70	3.1	3.2	2.3±0.80	2.3+	220±34	201±36
(7)	76–160	41.2	41.3	2.1±0.20	2	170±12	162±2
$ZnS_2O_6 \cdot 6\,H_2O$							
(3)	36–63	10.8	10.7	0.9±0.23	1	130±10	128±9
(4)	65–86	10.8	11.0	1.4±0.15	1	213±17	202±11
(5)	105–162	30.0	30.4	–°	–°	–°	–°
$CdS_2O_6 \cdot 4\,H_2O$							
(8)	30–66	10.4	10.1	1.0±0.10	1	121±20	118±19
(9)	70–135	10.4	10.2	0.9±0.09	4/3	96±12	98±13
(10)	163–220	18.6	18.6	0.0±0.00	0	–*	46±6

[a] Reich and Stivala method (Ref. 8).
[b] Coats and Redfern method (Ref. 7). Increments of 1/3 used for *n* determinations.
* Since the values obtained were inconsistent, average values are not included.
° Values are not included because reaction – (5) does not follow the rate law used for the Zn compound.
\+ Average value of several determinations.

with oxygen atoms in $S_2O_6^{2-}$ by means of hydrogen bonding, as indicated by the IR spectra. If the $S_2O_6^{2-}$ ions are coordinated to the metal ion, the uncoordinated oxygen atoms of $S_2O_6^{2-}$ are thereby held in a close proximity to coordinated H_2O which facilitates proton transfer and ultimate loss of SO_2 and H_2O simultaneously. As our previous study shows the alkali and alkaline earth metal ions are not as strongly hydrated and H_2O can be lost more easily without causing the $S_2O_6^{2-}$ decomposition that occurs at higher temperatures with higher activation energies [9].

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Zusammenfassung — TG- und DTG-Untersuchungen von $CoS_2O_6 \cdot 4\,H_2O$, $NiS_2O_6 \cdot 6\,H_2O$, $CuS_2O_6 \cdot 3.5\,H_2O$, $ZnS_2O_6 \cdot 6\,H_2O$ und $CdS_2O_6 \cdot 4\,H_2O$ wurden ausgeführt. Nach partieller Dehydratisierung geben die Dithionate von Co(II), Ni(II), Cu(II) und Zn(II) im letzten Schritt des Abbaus gleichzeitig Wasser und Schwefeldioxid unter Bildung der stabilen Metallsulfate ab. $CdS_2O_6 \cdot 4\,H_2O$ wird in den ersten beiden Zersetzungsschritten unter Abgabe von je 2 Wassermolekülen vollständing zersetzt. Im dritten Schritt wird nur SO_2 unter Bildung von $CdSO_4$ abgegeben. Kinetische Parameter dieser Reaktionen werden angegeben.

Резюме — Методом ТГ и ДТГ были изучены соединения $CoS_2O_6 \cdot 6\,H_2O$, $NiS_2O_6 \cdot 6\,H_2O$, $CuS_2O_6 \cdot 3.5\,H_2O$, $ZnS_2O_6 \cdot 6\,H_2O$ и $CdS_2O_6 \cdot 4\,H_2O$. После частичной дегидратации, дитионаты кобальта, никеля, меди и цинке теряют одновременно воду и двуокись серы, давая на конечной стадии разложения стабильные сульфаты металлов. Тетрагидрат дитионата кадмия полностью дегидратируется на первых двух стадиях разложения, теряя на каждой стадии по две молекулы воды. На третьей стадии соединение теряет только двуокись серы, давая сульфат кадмия. Приведены кинетические параметры реакций.