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THE THERMAL DECOMPOSITION OF DISODIUM PROPAN-2-ONE-1,3-DISULPHONATE

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The thermal decomposition of disodium propan-2-one-1,3-disulphonate ($NaO_3S.CH_2.CO.CH_2.SO_3Na$) in atmospheres of both oxygen and nitrogen proceeded by a complete molecular disruption with sodium sulphate or mixtures of sodium sulphate and sodium carbonate as the final residues. No organic compounds were detected in the volatile products.

Although a considerable amount of work has been reported on the thermal decomposition of salts of many types of carboxylic acids, no work has previously been reported on the decomposition of salts of sulphonic acids of ketones. In this study disodium propan-2-one-1, 3-disulphonate ($NaO_3S.CH_2.CO.CH_2SO_3Na$) has been heated in dynamic atmospheres of both oxygen and nitrogen to ascertain the decomposition route and to study the effect of heating rate on that route. Since it is well known that experimental conditions can have a large effect on the mode of decomposition of organic materials, every attempt was made to standardise conditions as much as possible. In all of the experiments the same finely ground sample was used, and the degree of packing in the crucibles was kept as similar as possible. Platinum crucibles were used for all experiments on the Stanton Redcroft TG750 thermobalance, and conical fused alumina crucibles of 2 cm^3 capacity on the other thermobalances.

Experimental

Sample preparation

Disodium propan-2-one-1, 3-disulphonate has previously been prepared by Grot [1]. In this study the compound was made from the corresponding diammonium salt, which was supplied, in 99.95% purity, by ICI Ltd., Agricultural Division, Billingham, England. One mole of the diammonium salt was dissolved in carbon dioxide free distilled water, two moles of sodium hydroxide added and the mixture heated under reflux in an atmosphere of nitrogen until ammonia ceased to be evolved. The resulting clear solution was cooled and the disodium salt precipitated by adding acetone. The product was removed by filtration, washed with acetone, and dried at 100°.

Equipment

The decomposition was studied using a Stanton Redcroft TG750 thermobalance, a Stanton Redcroft Automatic thermo-recording balance and a Stanton Redcroft Massflow vacuum and gas atmosphere thermobalance. The X-ray powder diffraction of the residues was carried out using a Siemens Kristalloflex 4 generator and a Siemens Diffractometer (Type F). The sulphur dioxide evolved during the decompositions using the Massflow thermobalance was determined by passing the evolved gases through bubblers and titrating with a standard solution of iodine using starch as indicator. A more detailed examination of the volatile fragments was obtained using a Hitachi RM11 6D Mass Spectrometer with an electron impact source, coupled to an F11 Perkin Elmer gas liquid chromatograph.

Results and discussion

The detailed results from the thermogravimetric studies are shown in Table 1 and typical TG curves are drawn in Figs 1 and 2. The results from the mass spectral study are shown in Fig. 3.

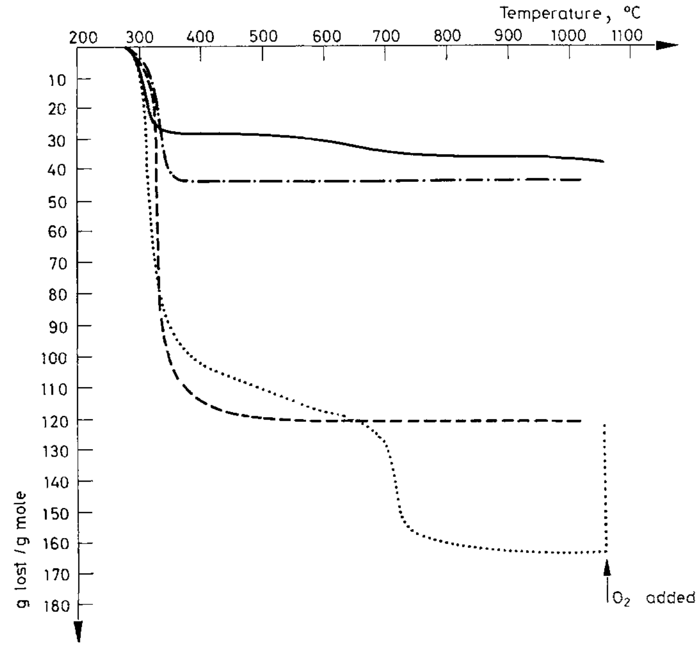

Fig. 1. The thermal decomposition of $NaO_3SCH_2COCH_2SO_3Na$ using a Stanton massflow thermobalance; ...... g lost/g mole in N_2 then O_2 ——— g SO_2 lost/g mole in N_2 then O_2; - - - - - g lost/g mole in O_2 – . – . – g SO_2 lost/g mole in O_2

When it was heated in a dynamic atmosphere of oxygen disodium propan-2-one-1, 3-disulphonate underwent a rapid decomposition between 350° and 450°, and the final product was sodium sulphate. Any carbon which was deposited during the most rapid changes of the decomposition was easily removed as carbon dioxide so that the residues were white.

Most of the experiments were carried out either in a dynamic atmosphere of nitrogen, or in nitrogen until there was no further change in mass followed by the addition of oxygen at high temperatures. Under these conditions there were three main stages in the decomposition.

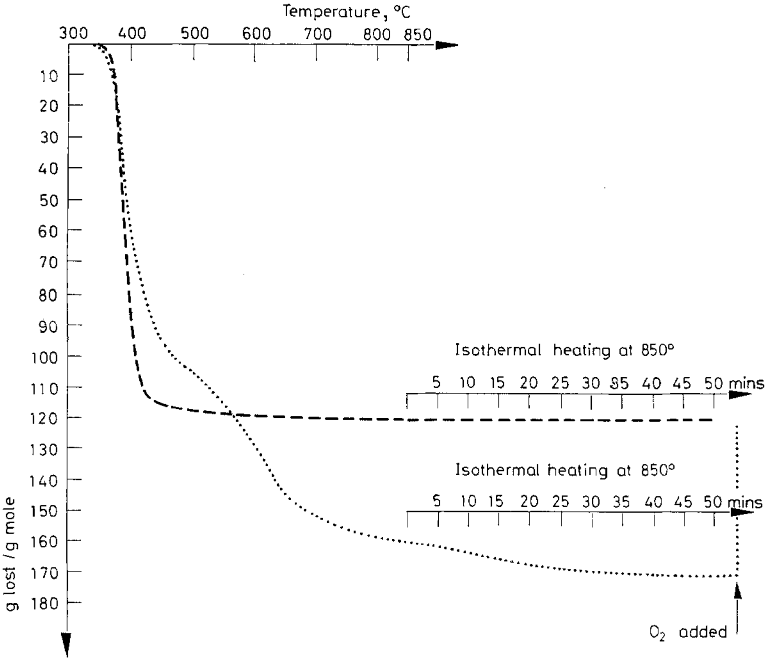

Fig. 2. The thermal decomposition of NaO$_3$SCH$_2$COCH$_2$SO$_3$Na using a Stanton TG 750 thermobalance; . . . . . . g lost/g mole in N$_2$ then O$_2$; – – – – g lost/g mole in O$_2$

Stage 1: This occurred over the same temperature range as when the samples were heated in oxygen, but during this change carbon was deposited and the samples went black. Nearly all the sulphur dioxide was evolved during this change.

Stage 2: On further heating in nitrogen the carbonaceous material was oxidized by some of the sulphate formed in Stage 1 and a slow, followed by a more rapid loss in mass, was observed. Only traces of sulphur dioxide were evolved, the loss in mass being due to oxides of carbon and possibly small amounts of water. During this change visual observation showed that the bulk of the carbonaceous material was removed. The residues at the end of this stage were pale grey in

Table 1

Results from the thermal analysis of disodium propan-2-one-1,3-disulphonate

Headings for columns in table

1. Equipment used
2. Atmosphere
3. Flow rate of gas ($cm^3 min^{-1}$)
4. Heating rate (°C min^{-1})
5. Weight of sample (mg)
6. g lost per mole during first stage
7. g lost per mole during second stage
8. Total g lost per mole in nitrogen
9. g gain per mole on adding oxygen
10. Total g lost per mole during decomposition
11. Moles of carbon deposited per mole during first stage
12. Moles of sodium salt decomposing to Na_2SO_4 per mole of sodium salt
13. g SO_2 lost per mole
14. Phases in residues detected with X-rays
15. Anions in residues detected by qualitative analysis

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	N_2	10	50	9.85	105.0	55.5	160.5							SO_4^{-2} S^{-2}
A	N_2	10	10	9.65	103.2	51.1	154.3							SO_4^{-2} S^{-2}
A	N_2 then O_2	10	100	9.75	107.8	39.7	147.5	24.3	123.2	1.28	0.91			SO_4^{-2} CO_3^{-2}
A	N_2 then O_2	10	50	9.45	104.0	63.5	167.5	44.2	123.3	1.61	0.91			SO_4^{-2} CO_3^{-2}
A	N_2 then O_2	10	20	9.30	99.8	22.0	121.8	1.5	120.3	1.71	0.99			SO_4^{-2}
A	N_2 then O_2	10	20	9.80	103.0	27.0	130.0	9.8	120.0	1.43	0.99			SO_4^{-2}
*A	N_2 then O_2	10	15	9.50	104.6	66.3	170.9	46.2	124.7	1.68	0.87			SO_4^{-2} CO_3^{-2}
A	N_2 then O_2	10	10	9.70	102.7	57.7	160.4	35.7	124.7	1.83	0.87			SO_4^{-2} CO_3^{-2}
A	N_2 then O_2	10	5	9.30	101.8	55.8	157.4	29.9	127.7	2.16	0.79			SO_4^{-2} CO_3^{-2}

A	N_2 then O_2	10	2	9.95	101.5	46.6	148.1	19.2	128.9	2.28	0.75			SO_4^{-2} CO_3^{-2}
A	O_2	10	50	9.75					121.2		0.97			SO_3^{-2}
*A	O_2	10	15	9.60					120.8		0.98			SO_4^{-2}
A	O_2	10	5	9.85					121.3		0.96			SO_4^{-2}
B	N_2	100	6.7	865.6	105.1	62.8	167.9					Na_2SO_4 Na_2S	Na_2SO_4 Na_2S	SO_4^{-2} S^{-2}
B	O_2	100	1.7	497.8					123.3		0.91	Na_2SO_4	Na_2SO_4	SO_4^{-2} CO_3^{-2}
B	N_2 then O_2	100	6.7	372.6	114.5	34.1	148.6	23.6	125.0	0.88	0.86		Na_2SO_4 Na_2SO_4	SO_4^{-2} CO_3^{-2}
**C	O_2	100	6.7	222.4					120.3		0.99	47.9	Na_2SO_4	SO_4^{-2}
**C	N_2 then O_2	100	6.7	203.6	110.3	53.5	163.8	40.9	122.9	1.05	0.92	37.5	Na_2SO_4	SO_4^{-2} CO_3^{-2}
C	N_2 then O_2	100	1.7	286.4	100.1	70.2	170.3	46.4	123.9	1.98	0.89	36.2	Na_2SO_4	SO_4^{-2} CO_3^{-2}

A = Stanton Redcroft TG 750 thermobalance
B = Stanton Redcroft Automatic thermo-recording balance
C = Stanton Redcroft Massflow vacuum and gas atmosphere thermobalance
* Decomposition curves shown in Fig. 2
** Decomposition curves shown in Fig. 1

solour and X-ray powder diffraction and qualitative analysis showed that sodium culphate and sodium sulphide were present.

Stage 3: Finally, when constant weight in nitrogen had been achieved, oxygen was added to remove any remaining carbon as carbon dioxide and to oxidize the sulphide formed in Stage 2 back to the sulphate. These three stages are the basis of the method of calculation of the results shown in Table 1.

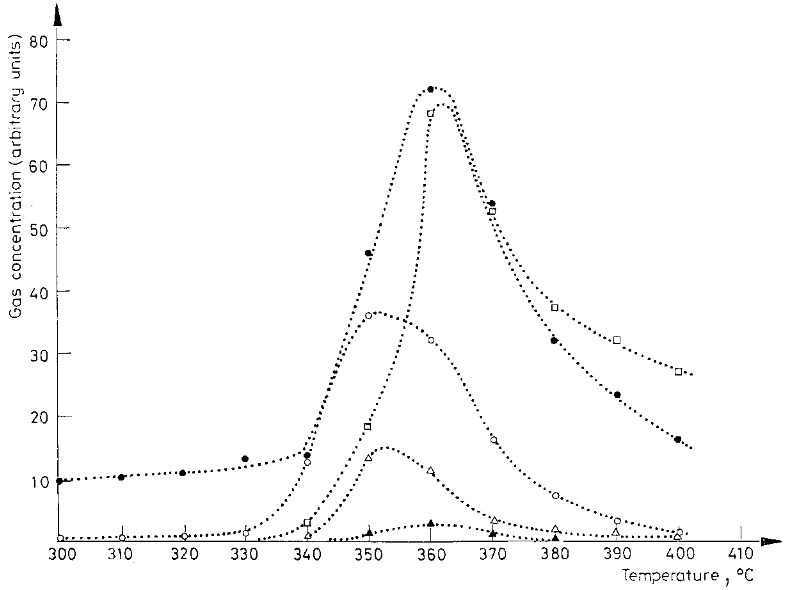

Fig. 3. Mass spectral analysis of the evolved gases. The thermal decomposition of $NaO_3SCH_2COCH_2SO_3Na$; ● ··· ● H_2O; □ ··· □ CO_2; ○ ··· ○ SO_2; △ ··· △ SO; ▲ ··· ▲ CS_2

Method of calculation

Stage 1: From 1 mole of $Na_2O_3SCH_2COCH_2SO_3$ let x mole decompose to give

Na_2SO_4, $(1-x)$ mole decompose to give
Na_2CO_3 and y mole of carbon be deposited.

Then residue at end of Stage 1 $= x Na_2SO_4 + (1-x) Na_2CO_3 + y C$
Volatiles lost during Stage 1 $= x[SC_3H_4O_3] + (1-x)[S_2H_4C_2O_4] - yC$
Therefore g lost/mole in Stage 1 $= 156 - 36x - 12y$

Stage 2: Let b mole of the deposited carbon be oxidized to CO_2 and CO by the Na_2SO_4 with the formation of Na_2S.

If c mole of carbon produce CO_2
Then $(b - c)$ mole of carbon produce CO
Therefore g lost/mole in Stage 2 $= 286 + 16c$

Stage 3: On adding oxygen $(y - b)$ mole of carbon are removed and the Na_2S produced in Stage 2 is reoxidized to Na_2SO_4.

Therefore g gain/mole in Stage 3 $= 286 + 16c - 12y$.

Note: After heating in oxygen, or heating in nitrogen followed by oxygen, the total g lost/mole $= 156 - 36x$.

The results from the thermogravimetry show that disodium propan-2-one-1, 3-disulphonate on heating in nitrogen followed by oxygen produces sodium sulphate which generally contains some sodium carbonate. It is also clear from the results using the same equipment that the proportion of sodium carbonate in the final residues increases as the heating rate is decreased. Similarly the amount of carbon deposited in Stage 1 also increases with decreasing heating rate. The latter observation is due to increased cracking of unstable organic compounds with longer residence within the interstices of the sample, and similarly the length of time that carbon dioxide is within the same sample may increase the amount of sodium carbonate formed. The temperature of the first stage in the decomposition as observed in the mass spectral analysis of the evolved gases is slightly lower than that observed in the thermogravimetry studies due to the different instrument conditions. The only identifiable species, in order of relative abundance, were H_2O, CO_2, SO_2, SO, CO, CS_2 and traces of COS. SO_2 and SO were evolved simultaneously, slightly preceding the major evolution of H_2O and CO_2. It is probable that SO arises by reduction of SO_2, rather than by the decomposition of some very unstable organic compound, both because of the similarity of the observed evolution patterns of SO_2 and SO, and because no evidence was found for any organic material in the volatile fragments. In addition no organic compounds were detected from larger scale experiments in which the disodium salt was heated in a dynamic atmosphere of nitrogen using a tube furnace, and where the effluent gas was passed through traps cooled with acetone and solid carbon dioxide.

The detection of CO, CS_2 and COS in the volatile fragments helps to explain the results from the Massflow thermobalance where the sulphur found in the sulphur dioxide evolved and in the sodium sulphate residue was always less than the total amount of sulphur in the starting material.

The decomposition routes can be summarized as follows:

1. Decomposition in oxygen

$$NaO_3S.CH_2.CO.CH_2.SO_3Na \xrightarrow{O_2} Na_2SO_4 + SO_2 + 3CO_2 + 2H_2O.$$

2. Decomposition in nitrogen followed by oxygen

Stage 1. $NaO_3S.CH_2.CO.CH_2.SO_3Na \xrightarrow{N_2} xNa_2SO_4 + (1-x)Na_2CO_3 + yC +$ $+$ volatile material

Stage 2. $xNa_2SO_4 + (1-x)Na_2CO_3 + yC \xrightarrow{N_2} xNa_2S + (1-x)Na_2CO_3 +$ $+ (y-b)C + cCO_2 + (b-c)CO$

Stage 3. $xNa_2S + (1-x)Na_2CO_3 + (y-b)C \xrightarrow{O_2} xNa_2SO_4 + (1-x)Na_2CO_3 +$ $+ (y-b)CO_2$

Conclusion

The results have shown that when heated in a dynamic atmosphere of oxygen disodium propan-2-one-1,3-disulphonate decomposed by a complete molecular disruption in the region of 350°–450°, and that the final product was sodium sulphate. In a dynamic atmosphere of nitrogen the first stage of the decomposition occurred over the same region, but carbon was deposited in the sodium sulphate formed. On further heating in nitrogen some of the sodium sulphate was reduced to sodium sulphide by the deposited carbon, and the final product, after addition of oxygen, was either sodium sulphate or a mixture of sodium sulphate with lesser amounts of sodium carbonate. No evidence could be found for the presence of organic compounds in the volatile material evolved.

Reference

1. W. G. Grot, J. Org. Chem., 30 (1965) 515.

RÉSUMÉ — La décomposition thermique du disulfite de sodium 1,3 one 2 propane ($NaO_3S.CH_2.CO.CH_2.SO_3Na$) s'effectue avec disruption moléculaire complète et obtention de résidus constitués de sulfate de sodium ou de mélanges de sulfate de sodium et de carbonate de sodium, tant en atmosphère d'oxygène que d'azote. Aucun composé organique n'est détecté dans les produits volatils.

ZUSAMMENFASSUNG — Die thermische Zersetzung des Dinatriumpropan-2-on-1,3-disulfonats ($NaO_3S.CH_2.CO.CH_2.SO_3Na$) vollzog sich sowohl in Sauerstoff- als in Stickstoff-Atmosphäre unter vollständiger Zerstörung des Moleküls mit Natriumsulfat oder Mischungen von Natriumsulfat und Natriumcarbonat als Restprodukt. Unter den flüchtigen Produkten wurden keine organischen Verbindungen nachgewiesen.

Резюме — Термическое разложение динатрий-пропан-2-он-1,3-дисйльфоната ($NaO_3S.CH_2.CO.CH_2.SO_3Na$) в атмосфере кислорода и азота протекает через стадию полного молекулярного разрыва с образованием сульфата натрия или смесей сульфата натрия и карбоната натрия в качестве конечных продуктов. Органических соединений в летучих продуктах реакции не обнаружено.