

REACTIONS OF CHROMATES AT HIGH TEMPERATURES

PART XX—SYNTHESIS AND DECOMPOSITION OF STRONTIUM CHROMATE

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INTRODUCTION

It has been shown in the previous investigation that the decomposition of calcium chromate to calcium chromite is an irreversible reaction. The basic chromate $12\text{CaO} \cdot 8\text{Cr}_2\text{O}_3$ is formed by the reaction between CaCr_2O_4 and $2\text{CaO} \cdot \text{Cr}_2\text{O}_3$ with the reduction of the latter to $\text{CaO} \cdot \text{Cr}_2\text{O}_3$ and to Cr_2O_3 in succession. The basic chromate decomposes in stages into calcium chromium chromates. The object of this investigation is to study the properties of strontium chromate at high temperature in order to confirm the mechanism suggested for the reaction occurring in the decomposition of calcium chromate and accordingly to assign structural formulæ to the compounds obtained in the decomposition of strontium chromate.

The results on the oxidation of chromic oxide in presence of strontium oxide also support the conclusion of the previous investigation that the oxidation of chromic oxide in presence of base, takes place with the formation of stable basic chromium chromates at intermediate stages of oxidation.

EXPERIMENTAL

The apparatus and the experimental procedure was the same as employed in the previous investigations.

Strontium chromate was prepared by the same method employed previously (This Journal 1938, **21A**, 159, 1939, **22A**, 111) by precipitating the salt from a solution of strontium chloride by potassium chromate. The chromate was 99.7% pure.

Decomposition of Strontium chromate—Decomposition of strontium chromate started at about 600° in vacuum. The gas initially evolved produced low pressures which were not reproduced on removing portions of the gas from the system. The decomposition

was then carried out at 1000°, when the pressure of oxygen continuously increased with time at constant temperature. The average rates of change in pressure values at different times are shown in table I

TABLE I

Time		Rate of change in pressure in mm per 5 mins
hrs	mins	
0		0.2
0	30	0.25
1		0.48
4	30	1.08

It is evident that the rate of decomposition as made out by pressure measurements also increases with time. Further experiments also showed that the rate of decomposition of the chromate also increases with rise in temperature. The reaction is thus one way and irreversible and autocatalytic. As the final product on complete decomposition is strontium chromite the reaction may be due the decomposition of SrCrO_4 into $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$, in accordance with the suggestion made previously in explaining the reactions of calcium chromate.

In analogy with the results on the decomposition of calcium chromate the formation of $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$ by the reaction between strontium chromate and strontium oxide supplied by the chromite $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$, is also possible. But in as much as the formation of basic strontium chromate out of strontium chromate and strontium oxide is an equilibrium reaction (*cf* part XVI), only a limited amount of $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$, can exist in the reaction products at any stage during the course of the reaction. Thus if system is left undisturbed it gets saturated with respect to $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$, in a short time and reaction proceeds with complete decomposition of the chromate to the chromite.

On the contrary if on account of continual removal of oxygen, the system undergoes variation in the concentration of the different phases, particularly in that of the basic chromate produced, the concentration of which is fixed by equilibrium constant of the reaction between the chromate and the oxide, the reaction proceeds with more and more formation and subsequent decomposition of $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$, and the ultimate products of the reaction contain the stable strontium chromium chromates.

A confirmation of the above suggestions was obtained by rapid decomposition of strontium chromate by continuous withdrawal of oxygen given out. At about 50% stage in the decomposition, no further evolution of gas was observed at 1060° , indicating the formation of a very stable compound. A support to these conclusions can also be obtained in the comprehensive study made by Athavale and Jatkari (*Ibid.*, 1938, 21A, 159) on the decomposition of strontium chromate. Their results indicate the existence of the stable strontium chromium chromates at 50%, 66.6% and 75% stages of the decomposition of strontium chromate, the corresponding compounds possessing characteristic decomposition pressures. It will be noticed that if the whole of strontium oxide present in strontium chromite ($2\text{SrO} \cdot \text{Cr}_2\text{O}_3$) is available for the formation of $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$, a larger proportion of the basic chromate is produced at a comparatively lower stage in the decomposition of strontium chromate and the decomposition of the basic chromate is complete at 50% stage with the formation of $12\text{SrO} \cdot 6\text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, which is completely soluble in acids, the acid insoluble portion being the chromic oxide phase in the system. In general, this is not possible as complete conversion of the basic chromite $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$ to Cr_2O_3 may not take place in as much as the reverse formation of $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$ and $\text{SrO} \cdot \text{Cr}_2\text{O}_3$ from Cr_2O_3 and SrO is also likely and usually the acid insoluble portion consists of Cr_2O_3 together with $\text{SrO} \cdot \text{Cr}_2\text{O}_3$. The results of Athavale and Jatkari thus show a great variation in the composition of the acid insoluble portions of the system particularly at the 50% stage, the composition of the corresponding acid soluble phase in the system indicating the existence of either $12\text{SrO} \cdot 6\text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$ alone or together with strontium chromate.

At higher temperature and at higher stages of decomposition the acid insoluble phase consists of pure $\text{SrO} \cdot \text{Cr}_2\text{O}_3$. The compounds formed at 66.6% and 75% decomposition of strontium chromate are therefore $9\text{SrO} \cdot 4\text{Cr}_2\text{O}_3$, Cr_2O_3 , and $6\text{SrO} \cdot 2\text{Cr}_2\text{O}_3$ in accordance with the conclusions of the decomposition of calcium chromate. The decomposition pressures measured by Athavale and Jatkar at 50%, 66.6%, and 75% stages in the decomposition of strontium chromate are due to the decomposition of $12\text{SrO} \cdot 6\text{Cr}_2\text{O}_3$, Cr_2O_3 , $9\text{SrO} \cdot 4\text{Cr}_2\text{O}_3$, and $6\text{SrO} \cdot 2\text{Cr}_2\text{O}_3$, which are present as separate phases at the corresponding stages. The existence of $15\text{SrO} \cdot 6\text{Cr}_2\text{O}_3$ is not indicated in their results probably owing to the different basic chromium chromates having similar stability ranges. The formulae suggested by Athavale and Jatkar for all the compounds were based upon the composition of the total solid phase and must now be modified.

The irreversibility of the reaction when the system is left to itself, was not observed by them at low temperature when the rate of decomposition is very slow. The complete decomposition of strontium chromate to the chromite above 1200° , attributed by them to the melting of strontium chromate at that temperature, is obviously due to the irreversible decomposition of strontium chromate, which is appreciably rapid at 1200° .

Decomposition of a mixture of strontium chromate with chromic oxide—Unlike in the decomposition of the mixtures of calcium chromate with chromic oxide, the addition of chromic oxide suppresses the decomposition pressures and lowers the extent of the decomposition of strontium chromate at 1060° .

A mixture of strontium chromate with chromic oxide (1:1 mols) was heated in vacuum. The decomposition pressures are given in table IV.

TABLE IV

Temp. $^\circ\text{C}$...	976	1003	1013	1059
Pressure mm	.	1.12	2.20	2.60	2.92

The decomposition pressures are lower than those for strontium chromate given by Athavale and Jalkar, the higher values obtained by them being due to the progressive decomposition of strontium chromate. The decomposition pressures continuously dropped down on decomposition. On evacuation to 0.5 mm pressure at 1060°, the decomposition reached about 33% stage. Keeping the system at that temperature for one hour showed no rise in pressure. From the results it appears that a larger proportion of basic chromate SrOCr_2O_7 CrO_3 is produced by the combination of strontium chromate and chromic oxide which forms a stable solid solution with $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_7$.

As in the decomposition of strontium chromate the system at several stages consisted of chromic oxide as well as strontium oxide and oxygen it was proposed further to investigate the oxidation of chromic oxide in presence of strontium oxide.

Oxidation of a mixture of chromic oxide with 3 mols of strontium carbonate—A mixture of chromic oxide with strontium carbonate (1.3 mols) was heated in vacuum. The decomposition started below 550°. The decomposition pressures of the mixture are given in table III and correspond to those of strontium carbonate.

TABLE III

Temp °C	Pressure mm	Temp °C	Pressure mm
774	1.44	921	10.20
835	1.76	933	14.40
874	3.16	962	28.46
891	5.52	1012	35.44

The carbonate was completely decomposed. Oxygen was then admitted into the apparatus and the oxidation proceeded in stages. The decomposition pressure measurements showed that at all the stages a side formation of some unstable compound though in minute quantities occurs along with the formation of the stable chromium chromates. The system at the different stages did not show evolution

of oxygen when the unstable product was decomposed completely at 1050° indicating that major portion of the reaction occurs with the formation of strontium chromium chromates. Beyond the 75% stage the further oxidation did not proceed at high temperature and oxygen was absorbed very slowly even at low temperatures.

The decomposition pressure of the product on complete oxidation are given in table IV, which indicate the existence of $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$ and $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$ in the product similar to the behaviour of the oxidation of chromic oxide in presence of calcium oxide in like circumstances.

TABLE IV

Temp °C	626	678	711	763	784
Pressure mm	2.40	4.62	6.60	11.12	13.32

The decomposition pressures are very low as compared to the vapour pressures of $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$ (*cf* part XVI) and point out to the production of $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$ in very small amount. The experiments thus indicate that $4\text{CaO} \cdot \text{Cr}_2\text{O}_3$ is also produced along with $3\text{CaO} \cdot \text{Cr}_2\text{O}_3$, but as the oxidation of the former to $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$ does not take place at higher temperature and proceeds very slowly at low temperature, the major reaction in the oxidation of chromic oxide in presence of strontium oxide occurs with the oxidation of $3\text{SrO} \cdot \text{Cr}_2\text{O}_3$ and with the formation of stable chromium chromates.

Strontium chromite $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$ can be prepared by the decomposition of strontium chromate at 1030°. It was observed that this chromite does not absorb oxygen at any temperature between 25° and 1030°.

The results of this investigation point out to the possibility of the existence of four chromites viz, $\text{SrO} \cdot \text{Cr}_2\text{O}_3$, $2\text{SrO} \cdot \text{Cr}_2\text{O}_3$, $3\text{SrO} \cdot \text{Cr}_2\text{O}_3$ and $4\text{SrO} \cdot \text{Cr}_2\text{O}_3$, which can be distinguished by the study of their oxidation products.

SUMMARY

Strontium chromate decomposes to strontium chromite, the reaction being irreversible and autocatalytic. On rapid decomposition, the basic chromate $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$ is produced and subsequently decomposes into strontium chromium chromates, viz., $12\text{SrO} \cdot 6\text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, $9\text{SrO} \cdot 4\text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, $15\text{SrO} \cdot 6\text{Cr}_2\text{O}_3 \cdot 2\text{Cr}_2\text{O}_3$, and $6\text{SrO} \cdot 2\text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, all the compounds possessing characteristic decomposition pressures.

The addition of chromic oxide suppresses the decomposition of strontium chromate by producing another basic chromate $\text{SrO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$, which forms a stable solid solution with $12\text{SrO} \cdot 8\text{Cr}_2\text{O}_3$.

The oxidation of chromic oxide in presence of strontium oxide takes place mainly with the formation of stable strontium chromium chromates at the intermediate oxidation stages.

The results of this investigation also point out to the possibility of the existence of four basic chromites viz., $\text{RO} \cdot \text{Cr}_2\text{O}_3$, $2\text{RO} \cdot \text{Cr}_2\text{O}_3$, $3\text{RO} \cdot \text{Cr}_2\text{O}_3$ and $4\text{RO} \cdot \text{Cr}_2\text{O}_3$, which can be distinguished by the study of properties of their oxidation products.

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