

XII.—*The Slow Decomposition of Ammonium Chromate, Dichromate, and Trichromate by Heat.*

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WHEN ammonium dichromate is heated at temperatures ranging from about 118° to 205° , instead of a sudden decomposition mainly to chromium sesquioxide, nitrogen, and water, such as occurs at higher temperatures, a slow change takes place accompanied with the evolution of ammonia, and a black substance remains. This decomposition has been previously noticed by E. Maumené (*Bull. Soc. chim.*, 1892, [iii], 7, 174), who found that the salt decomposed slowly at 204° , giving rise ultimately to chromium dioxide.

The author has examined this slow decomposition of the chromates of ammonium (for the trichromate and chromate undergo similar changes), and found, some two years ago, that the final product in the case of the dichromate was a hydrated chromium dioxide, and that ammonia was evolved continuously during the decomposition.

The exact composition of the final product is dealt with in this paper, and has also lately been determined by W. M. Hooton (*Proc.*, 1908, 24, 27), whose conclusions agree with those of the author, except as to the degree of hydration of the substance. The composition of this end-product does not, however, throw much light on the course of the reaction, as some of the oxygen it contains is absorbed from the air during the heating.

Examination of the Residue obtained by Heating Ammonium Dichromate in Air at 192° .—Weighed amounts of pure finely-powdered ammonium dichromate, dried at 100° , were heated in a V. Meyer bath,

various liquids being used as heating agents. At 182° (boiling aniline) the decomposition was very slow, whilst at 205° (boiling nitrobenzene) the rate of decomposition was much increased, but sooner or later the ordinary deflagration to chromium sesquioxide, nitrogen, and water took place. At 192° the slow decomposition occurred with sufficient rapidity, and the explosive decomposition did not supervene.

At this temperature the darkening of the salt was observable within a few minutes, and after two hours' heating the substance had become quite black. When large crystals were used instead of the finely divided powder, it was evident that decomposition had begun at the surface, leaving unaltered dichromate beneath.

The heating was continued for several days, until the product had reached an approximately constant weight. The weight decreased steadily at first, and then increased slightly. The residue was a black, amorphous, hygroscopic powder, slowly acted on by water, yielding chromic acid and hydrated chromium sesquioxide, and rapidly by alkalis, yielding the hydrated sesquioxide and a chromate. It did not contain nitrogen.

Six distinct samples were analysed, the results being given in table I. The active oxygen was in some cases determined iodometrically; in others, by decomposing with alkali and estimating the resulting chromate with ferrous salts. The sesquioxide was determined by ignition, and the water by direct weighing.

TABLE I.

No.	Cr ₂ O ₃ per cent.	Active oxygen per cent.	H ₂ O per cent.
1	84·42	8·98	6·74
2	84·06 ; 83·63	9·08	6·86
3	83·06 ; 83·02	9·18 ; 8·97 ; 9·01	6·54 ; 6·56
4	84·10 ; 84·41	8·88 ; 8·84	7·03 ; 7·22
5	—	9·02	7·50
6	84·45	—	—

3CrO₂,H₂O requires Cr₂O₃=84·46. O (active)=8·88 ; H₂O=6·66 per cent.

2CrO₂,H₂O requires Cr₂O₃=81·74. O (active)=8·59 ; H₂O=9·67 per cent.

The numbers thus agree fairly well with those required by the formula 3CrO₂,H₂O, and differ considerably from those required by the formula 2CrO₂,H₂O. The variations between the different samples are, however, larger than might be expected for a perfectly definite substance.

In order to eliminate oxidation by the air, and to discover, if possible, the intermediate stages of the decomposition, the dichromate,

trichromate, and the chromate were each heated in a stream of nitrogen at constant temperatures.

In each case the course of the decomposition was similar; nitrogen, ammonia, and water were evolved, and the salt rapidly became black. From this black substance, water extracted some unchanged salt, leaving an amorphous, insoluble, black residue, which yielded, on hydrolysis with alkali hydroxide, chromate, chromic hydroxide, and ammonia.

Three experiments (*A*, *B*, and *C*) were made with ammonium dichromate; in *A*, the salt was heated for four and a-half hours at an average temperature of 195.2° ; *B* was similar, except that the average temperature, 193.8° , was slightly lower, and *C* was made in nitrogen under about 20 mm. pressure. In this case the apparatus was altered slightly, the water and ammonia evolved being collected together in concentrated sulphuric acid, and the ammonia alone estimated.

Experiment *D* was made with the trichromate, $(\text{NH}_4)_2\text{Cr}_3\text{O}_{10}$, and *E* with the chromate, $(\text{NH}_4)_2\text{CrO}_4$; in detail they were similar to experiments *A* and *B*.

As the methods of estimation used in each case were similar, they are given below, in the account of the experiments with the dichromate. The black insoluble residues obtained after extraction with water of all unchanged salt from the product of each experiment were very similar in appearance and properties. Their compositions are given in table IV (p. 92).

Method of Heating.—The heating apparatus consisted of a large corked boiling tube containing methyl benzoate; through the cork passed a condenser and a test-tube. The latter was closed by an indiarubber stopper, through which passed a thermometer, the tube leading in the nitrogen, and that conducting out the water, nitrogen, and ammonia evolved. Inside this test-tube was placed a weighed quantity of the finely-powdered dichromate, contained in a short, wide tube provided with a loop of platinum wire, so that it could easily be removed from the heating apparatus.

The water evolved was collected in a U-tube containing solid potassium hydroxide, and, after its removal, the stream of nitrogen containing the evolved ammonia was led into a three-necked flask containing *N*/10-acid tinted with methyl-orange. The jet of a burette passed through one of the necks, so that a measured amount of acid could be added at any time. By this arrangement, the amount of ammonia evolved at any stage could be found, and, at the end of the experiment, the weight of water formed and the loss in weight of the dichromate also, giving, by difference, the weight of nitrogen evolved from the dichromate. As the amounts of ammonia evolved were small, a blank experiment was first made, proving that the apparatus was entirely free from ammonia.

The nitrogen used was prepared by dropping a concentrated solution of pure sodium nitrite into a slightly warmed solution of ammonium chloride, and purified by passing through wash-bottles containing ferrous sulphate solution, concentrated aqueous sodium hydroxide, concentrated sulphuric acid, and through two tubes containing red-hot copper. When an experiment was to be made, the nitrogen was driven from the gas-holder through a wash-bottle containing concentrated sulphuric acid, through a potash tower, and thence into the heating apparatus by means of a delivery tube, which came within 1 cm. of the surface of the dichromate, so that the products evolved should be removed as quickly as possible.

After each experiment, the black solid resulting from the decomposition of the salt was treated with water several times until practically nothing more was dissolved from it. Although water had a slight action on the insoluble part, it was not difficult to discover when all the soluble portion (proved to be unaltered ammonium dichromate by estimations of chromic acid and ammonia) had been extracted. For instance, in experiment *B*, extraction with water at the ordinary temperature for fifteen minutes withdrew 1.5912 grams of unaltered dichromate, whereas a further extraction, for the same length of time, removed an amount estimated to be not more than one milligram.

The insoluble portion, that is, the residue left by the dichromate that had undergone decomposition, was separated from the extracted unaltered salt by filtration in a Gooch crucible, and was then decomposed by boiling with sodium hydroxide in a current of steam, the evolved ammonia being determined by standard acid.

The other products of the action of sodium hydroxide, namely,

TABLE II.

Expt.	Time of heating in hours.	Temp.	Weight taken.	Weight decomposed.	Loss in weight.	Water evolved.	Ammonia evolved.	Nitrogen (by diff.).
<i>A</i>	4½	195.2°	3.2653	1.6376	0.3139	0.2135	0.0185	0.0819*
<i>B</i>	4½	193.8	2.3393	0.7481	0.1316	0.0832	0.0074	—
<i>C</i>	2½	195.0	1.4418	0.7410	0.1305	—	0.0109	—
<i>D</i>	3	194.7	3.4862	1.2776	0.1733	0.1179	0.0031	—
<i>E</i>	3	195.8	1.7270	all	0.5564	0.2721	0.1923	—

* The accuracy of this amount of nitrogen, obtained by difference, may be verified thus:

Total nitrogen originally present in 1.6376 grams of dichromate (this being the amount of the salt decomposed) = 0.1818 gram.

Nitrogen found in residue from this dichromate = 0.0839 gram.

Nitrogen evolved as NH_3 = 0.0152 gram: therefore nitrogen evolved in free state = 0.1818 - (0.0839 + 0.0152) = 0.0827 gram, a value which is in close agreement with the amount, 0.0819 gram, found as above.

sodium chromate and chromic hydroxide, were then separated by filtration, and the chromate determined by ferrous iron.

Details of each experiment are given in tables II and III; table IV contains the analyses of the insoluble residues.

The following numbers, representing c.c. of acid ($N/10 \times 1.055$) neutralised by the evolved ammonia in expt. *A*, show that it was evolved at a constant rate.

In first hour, 2.06; in second hour, 2.48; in third hour, 2.50; and in fourth hour, 2.33.

TABLE III.

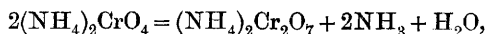
Expt.	Amount of decomposition of salt per 100 grams per hour.	Rate of evolution of NH_3 per 100 grams of salt per hour.	Ratio.
			$\frac{\text{Nitrogen evolved in free state.}}{\text{Nitrogen evolved as } \text{NH}_3.}$
<i>A</i>	11.15 grams.	0.126 gram.	5.4
<i>B</i>	7.11 ,,	0.070 ,,	5.7
<i>C</i>	19.44 ,,	0.250 ,,	4.2
<i>D</i>	12.22 ,,	0.030 ,,	20.8
<i>E</i>	—	—	0.56

From the figures given, it may be seen that rise of temperature and lowering of pressure have considerable effect in increasing the rate of decomposition of the dichromate, yet do not much influence the fraction of the contained nitrogen evolved as ammonia.

The rate of decomposition of the trichromate was greater than that of the dichromate, but, as might have been anticipated, much less of its nitrogen was evolved as ammonia.

In experiment *E*, on extracting the solid product of the decomposition with water, it was found that 98 per cent. of the chromate had been transformed into a black, insoluble residue, whilst 2 per cent. dissolved as ammonium dichromate.

It seemed probable that the ammonium chromate would be very rapidly decomposed into the dichromate, ammonia, and water according to the equation :



as this decomposition occurs slowly at the ordinary temperature and rapidly at 100° . After this supposed conversion into dichromate had taken place, the rest of the decomposition might be expected to be identical with that of the dichromate. This was partly confirmed by experiment, for it was found that the ammonia evolved during the first twenty-five minutes' heating neutralised 92.5 c.c. of acid; during the second twenty-five minutes, 13.0 c.c. of acid, and during the third twenty-five minutes, 1.8 c.c. of acid.

Thus, of the total amount of ammonia, 0.3860 gram, contained in the chromate used, 0.1923 gram, or almost exactly half, was evolved

as ammonia, and more than nine-tenths of this evolution took place during the first thirty minutes' heating.

The dichromate formed from the chromate, however, decomposed much more rapidly than the dichromate used in experiments *A*, *B*, and *C*. For example, in experiment *A*, after four and a-half hours' heating, only half of the salt had been transformed into the insoluble residue, whilst, in this case, three hours' heating at almost the same temperature had decomposed practically the whole of the salt.

It will be seen, also, in table IV that, although the dichromate and chromate residues were similar in properties, the chromate residue contained considerably more chromium sesquioxide,

Examination of the Insoluble Residues.—The solid residues, obtained by the decomposition of the salts in the foregoing experiments, were all black, amorphous solids, very similar in appearance. They were insoluble in water, but were slowly acted on by it to a slight extent, giving up chromium trioxide and ammonia. The residue from the trichromate was the most easily acted on by water, but the difference was not great. All were decomposed similarly, by boiling with aqueous sodium hydroxide, into sodium chromate, chromic hydroxide, and ammonia.

Experiments proved that these residues took up small amounts of water during the extraction of the unchanged salts, but in table IV the percentage compositions are those of the residues before this absorption of water had taken place.

TABLE IV.

Expt.	Composition in percentages of substances formed on hydrolysis.				Composition expressed in molecular ratios.			
	Cr ₂ O ₃ .	CrO ₃ .	NH ₃ .	H ₂ O.	Cr ₂ O ₃ .	CrO ₃ .	NH ₃ .	H ₂ O.
<i>A</i>	34·85	52·36	7·70	5·09	1·00	2·29	1·98	1·24
<i>B</i>	32·51	53·58	8·26	5·66	1·00	2·51	2·28	1·47
<i>C</i>	32·76	53·27	7·11	6·86	1·00	2·47	1·94	1·77
<i>D</i>	31·72	56·87	5·31	6·10	1·00	2·73	1·50	1·63
<i>E</i>	39·08	46·12	7·12	7·70	1·00	1·79	1·63	1·67

As stated above, these residues were slightly acted on by water, and consequently, in separating them from the unchanged salts, a very small amount of decomposition took place, but this was not sufficient materially to alter their compositions.

It will be seen that the dichromate residues do not differ much from one another in composition; in particular, those from experiments *B* and *C* have almost identical percentages of chromium sesquioxide and chromium trioxide, although these experiments were made under different conditions; these two residues likewise contain chromium sesquioxide, chromium trioxide, and ammonia in molecular ratios

which approach to simple whole numbers (2 : 5 : 4). The properties of these residues are not those of ammonium salts in general, for they are black, insoluble, and amorphous ; the production from them, on hydrolysis, of a chromate and ammonia may indicate possibly that they are mixtures of chromium sesquioxide, formed by the reduction of the chromium trioxide of the salts by the hydrogen of the ammonium radicle, with some substance, such as an amide, capable of yielding chromic acid and ammonia on hydrolysis, and produced by a simultaneous dehydration of the salt.

The evolution of ammonia at a uniform rate throughout the decomposition of the dichromate renders it unlikely that it is a secondary product formed, for instance, by the action of the basic sesquioxide produced by decomposition of part of the salt on the undecomposed portion.

A few experiments were also made in order to estimate the amount of ammonia evolved in the ordinary rapid decomposition of the dichromate, but the exact estimation was rendered difficult owing to the simultaneous production of oxides of nitrogen. In the experiments made, the nitrogen evolved as ammonia was always in excess of that evolved in the form of oxides.

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