Thermal Decomposition of Potassium Permanganate and Related Substances. Part III.[1] Direct Evidence that $K_3(MnO_4)_2$ is not an Intermediate Phase in the Thermal Decomposition of Potassium Permanganate in Air at *ca.* 200 °C

By **Frank H. Herbstein** * and **Aharon Weissman**, Department of Chemistry, Technion Israel Institute of Technology, Haifa, Israel

Continuous Debye–Scherrer *X*-ray diffraction photographs have been recorded of potassium permanganate samples over the temperature range 25—400—25 °C in air. These show that the only solid products are K_2MnO_4 and ' $K_4Mn_7O_{16}$,' thus refuting a previous conclusion that $K_3(MnO_4)_2$ is an intermediate phase in the thermal decomposition of $KMnO_4$.

It has been generally accepted [2,3] that the products of thermal decomposition of potassium permanganate in air at *ca.* 200 °C are K_2MnO_4, ' $K_4Mn_7O_{16}$ ' (a cryptomelane-like material whose composition and structure are not known in detail at present), and O_2 gas. However Boldyrev *et al.*[4] have recently suggested that crystalline $K_3(MnO_4)_2$ is formed in the first stages of the decomposition and that K_2MnO_4 is produced in a later stage. If this is indeed true, then all the earlier chemical and kinetic studies of thermal decomposition of $KMnO_4$ will have to be reinterpreted. We have therefore felt it desirable to check this suggestion by carrying out experiments which demonstrate unequivocally what solid phases are formed *in situ* during a thermal decomposition; the results show that $K_3(MnO_4)_2$ was not formed at any stage of our experiments and thus confirm

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[1] Part II, F. H. Herbstein, G. Ron, and A. Weissman, Proc. 3rd Internat. Conf. Thermal Analysis, Davos, Switzerland, 1971; *Thermal Analysis*, 1971, **2**, 281.

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[3] F. H. Herbstein, G. Ron, and A. Weissman, *J. Chem. Soc.* (*A*), 1971, 1821.

[4] V. V. Boldyrev, Z. G. Vinokurova, L. N. Senchenko, G. P. Shchetinina, and B. G. Erenburg, *Russ. J. Inorg. Chem.*, 1970, **15**, 1341.

the accepted description of the course of the thermal decomposition.

EXPERIMENTAL

Details of their experimental procedure were not given by Boldyrev *et al.*[4] and it is not clear whether their *X*-ray diffraction studies were made on samples held at the reaction temperature or after cooling to room temperature. As the decomposition products are unstable in air, it is essential that these should be studied *in situ* and at the reaction temperature. To this end we have designed and built a Debye–Scherrer type camera in which the diffraction pattern is registered continuously on moving film as the sample temperature is changed. In this way the diffraction patterns of the decomposition products are obtained directly and there is no possibility that artefacts are formed, as could happen during cooling of the sample and/or transfer from the reaction vessel to the *X*-ray diffraction camera.

The samples used were powdered potassium permanganate, packed into the ends of 0·3 mm thin-walled quartz capillary tubes and held in place (even during rather violent decomposition reactions) by a plug of loosely packed powdered glass. Although the capillaries were not sealed, contact with the atmosphere was poor, as was shown by the time taken for '$K_4Mn_7O_{16}$' to become hydrated (see below). The capillary tube was mounted on a standard goniometer head, adjusted to lie on the axis of the film holder, and inserted into a co-axial, spirally wound, platinum heater. Under these conditions, the capillary and powdered glass contributed only to the diffuse background of the diffraction pattern. Sample temperature was monitored in a separate experiment in which the sample was replaced by a thin-wire chrome–alumel thermocouple. Rates of heating and film progression were adjusted to give adequately exposed photographs which are unfortunately not suitable for reproduction because of lack of contrast. In the present experiments Fe-K_α radiation was used in order to increase the dispersion on the photograph and to reduce the fluorescent background.

The following temperature cycles are representative of those used in a number of experiments. (i) Sample heated to 375 °C at 0·3 °C min^{-1} and cooled to 25 °C at the same rate. (ii) Sample heated to 185 °C, held at 185 °C for 24 h, then heated further to 405 °C and cooled to 25 °C. Both heating and cooling was at the rate of 1 °C min^{-1}.

RESULTS AND DISCUSSION

The $KMnO_4$ pattern of sample (i) started to disappear at *ca.* 235 °C and had been completely replaced by a new pattern after an additional heating period of 100 min, *i.e.* by the time a temperature of 265 °C had been reached. The original and new patterns both appeared on the photograph over the temperature range 235—265 °C. The new pattern consisted of the stronger powder lines of K_2MnO_4[5] and a single line of '$K_4Mn_7O_{16}$' at $d = 6{\cdot}40$ Å. No change occurred on further heating. No change occurred on cooling but, after being set aside for *ca.* 5 h at room temperature, the line at 6·40 Å disappeared and was replaced by two lines at $d = 7{\cdot}09$ and 3·55 Å. This change has been shown to be due to absorption of water vapour from the atmosphere, with consequent change from '$K_4Mn_7O_{16}$' to '$K_4Mn_7O_{16},nH_2O$' (*n ca.* 5).[2] The $KMnO_4$ pattern from sample (ii) began to disappear after 9 h at 185 °C; during a further 2 h at 185 °C the patterns of $KMnO_4$, K_2MnO_4, and $K_4Mn_7O_{16}$ all occurred together. The $KMnO_4$ pattern had disappeared completely after 11 h at this temperature. No change occurred on further heating to 400 °C. On cooling the same behaviour was found as that for sample (i).

A rather similar experiment had earlier been carried out with $RbMnO_4$, using a high-temperature diffractometer as the camera described above was not then operative. The powdered $RbMnO_4$ sample was held at 230 °C for 20 min and then cooled to 150 °C, at which temperature its diffraction pattern was recorded. Changes in the diffraction pattern were observed only after two such cycles. A progressive diminution of the $RbMnO_4$ pattern occurred, together with growth of a peak at $d = 6{\cdot}86$ Å, due to '$Rb_4Mn_7O_{16}$,' and of the (211) and (031) peaks of Rb_2MnO_4 at $d = 3{\cdot}23$ and 3·10 Å respectively.

Thus we find that, for $KMnO_4$, only one change occurred in the diffraction pattern on heating ($KMnO_4 \longrightarrow K_2MnO_4 +$ '$K_4Mn_7O_{16}$') and only one change after cooling to 25 °C ('$K_4Mn_7O_{16}$' $\longrightarrow$ '$K_4Mn_7O_{16},nH_2O$'). The pattern of $K_3(MnO_4)_2$ was not encountered in our experiments. Analogous results were obtained with $RbMnO_4$.

CONCLUSION

The phase $K_3(MnO_4)_2$ is not an intermediate in the thermal decomposition of $KMnO_4$ in air at *ca.* 200 °C, but K_2MnO_4 and '$K_4Mn_7O_{16}$' are formed directly, as has been generally accepted. Similar conclusions hold for the $RbMnO_4$ system.

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