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NOTE

On the Question of the Existence of $K_3(MnO_4)_2$ as an Intermediate Phase in the Thermal Decomposition of Potassium Permanganate*

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Since Herbstein's work (*1*) has placed in doubt the results of our experiments (*2*), according to which the intermediate compound $K_3(MnO_4)_2$ is formed during the transition of potassium permangante into manganate, we have carried out special investigations for the purpose of proving experimentally the question about the existence of this compound.

To carry out the experiments, potassium permanganate which had been twice recrystallized from aqueous solution was placed as finely ground powder in a flat cuvette and heated in a high-temperature camera from 20 to 215°C. Heating time lasted about 5 min. For the identification of the phases existing in the specimen, which was carried out on a DRON-0.5 apparatus (radiation–CuK_α), a θ range of 11–18° was used, where, according to the set of diffraction maxima and the distribution of their intensities, it was possible to determine the phase composition unambiguously. Table I presents the X-ray characteristics of $KMnO_4$ and K_2MnO_4, which were derived from (*3*, *4*), as well as the characteristics of $K_3(MnO_4)_2$, which we prepared specially for the present investigation and used in the present work for identifying these materials.

The X-ray diagrams of the initial potassium permanganate and of the products formed in various consecutive stages of the thermal decomposition are shown in Fig. 1. As is clearly seen, a gradual change takes place during the course of the decomposition from the initial diffraction picture, which corresponds to pure potassium permanganate. A reflection at $\theta = 13.69°$, which corresponds to an interplanar spacing of 3.26 Å, becomes stronger and then predominant, while the intensity of a reflection at $\theta = 13.82°$ ($d = 3.22$ Å) decreases monotonically. The intensity of reflections $\theta = 11.92°$ ($d = 3.73$ Å) and $\theta = 12.44°$ ($d = 3.57$ Å) decreases, while the intensity of reflections 2.90 and 3.65 Å increases. In X-ray scans *b–f* of Fig. 1, a reflection at $\theta = 16.66°$ ($d = 2.68$ Å) appears; it is not overlapped for $K_3(MnO_4)_2$. $K_3(MnO_4)_2$ is very clearly established in the filming of the partially decomposed permanganate over the range of angles 18–19° and 20–21°, where reflections 2.44/10 and 2.16/37 correspond to this phase. X-Ray scans *e* and *f* characterize specimens which are practically pure $K_3(MnO_4)_2$ with an admixture of $KMnO_4$ and K_2MnO_4 (the characteristic reflection is 3.08 Å). In the course of further decomposition, reflections corresponding to $K_3(MnO_4)_2$ gradually decrease, at the same time that the reflections corresponding to the final product K_2MnO_4 increase. Thus, the formation of $K_3(MnO_4)_2$

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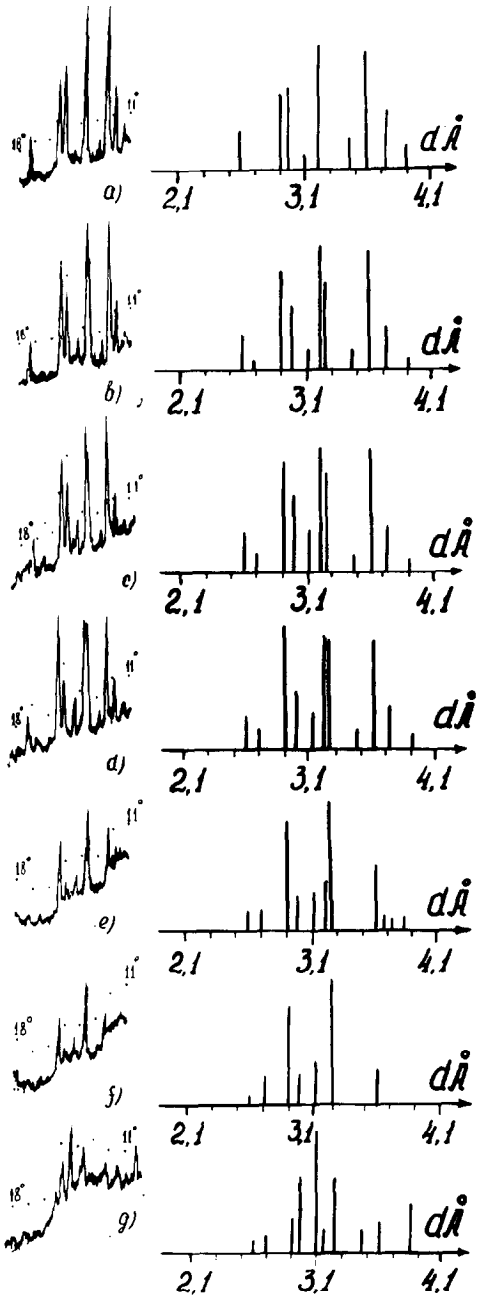
TABLE I
X-RAY DIAGRAM CHARACTERISTICS OF $KMnO_4$, $K_3(MnO_4)_2$, AND K_2MnO_4

θ_{Cu} (deg)	$KMnO_4$ (3)		$K_3(MnO_4)_2$		K_2MnO_4 (4)	
	d(Å)	I_{rel}	d(Å)	I_{rel}	d(Å)	I_{rel}
7.63	5.80	—	—	—	—	—
8.55	—	—	—	—	5.18	20
9.08	—	—	4.873	21	—	—
9.68	4.58	10	—	—	—	—
9.76	4.54	45	4.534	6	—	—
10.32	—	—	—	—	4.30	35
10.40	—	—	—	—	4.27	15
11.40	3.90	20	—	—	—	—
11.58	—	—	—	—	3.84	40
11.92	3.73	45	—	—	—	—
12.14	—	—	3.654	8	—	—
12.36	—	—	—	—	3.60	10
12.44	2.574	95	3.569	12	—	—
12.90	3.444	20	—	—	—	—
13.69	—	—	3.256	100	—	—
13.82	2.223	100	—	—	—	—
14.12	—	—	—	—	3.16	6
14.44	—	—	—	—	3.08	100
14.96	—	—	—	—	2.984	35
15.14	2.954	75	—	—	2.946	15
15.40	—	—	2.895	92	—	—
15.48	2.885	35	—	—	—	—
15.58	2.867	35	—	—	—	—
16.66	—	—	2.680	2	—	—
17.22	—	—	—	—	2.601	20
17.40	2.579	28	—	—	2.570	35
18.04	—	—	—	—	2.488	30
18.40	—	—	2.436	10	—	—
18.88	—	—	2.376	12	—	—
19.06	2.358	1	—	—	—	—
19.48	2.310	1	—	—	—	—
19.60	—	—	—	—	2.296	14
19.68	—	—	—	—	2.288	6
19.74	—	—	—	—	2.281	6
19.83	—	—	2.266	2	—	—
19.88	—	—	—	—	2.265	6
20.42	2.206	31	—	—	—	—
20.68	2.181	44	—	—	—	—
20.82	—	—	2.163	37	—	—
20.98	—	—	—	—	2.151	16
21.16	—	—	—	—	2.136	6
21.95	—	—	—	—	2.061	35
22.97	—	—	1.970	25	—	—
23.60	1.924	10	—	—	1.922	12
24.46	1.857	14	—	—	—	—
24.71	1.843	14	—	—	—	—
24.76	1.839	12	1.835	2	—	—
24.92	—	—	—	—	1.828	4
24.98	1.824	20	—	—	1.824	5
25.08	—	—	1.814	2	—	—



as an intermediate product of thermal decomposition of $KMnO_4$ can be considered to be a firmly established experimental fact.

The possibility of identifying $K_3(MnO_4)_2$ among the thermal decomposition products depends on the conditions of the experiment. The temperature of 215°C was not chosen at random. It is precisely the temperature at which X-ray detectable concentrations of $K_3(MnO_4)_2$ are extremely great, both from the results of preliminary experiments of the present work as well as from the experiments conducted earlier in (*2*). High-temperature radiography in a non-isothermal system at temperatures of 185–260°C, which we carried out, indicated that the presence of $K_3(MnO_4)_2$ was uncertain to X-ray analysis. As a consequence of excessive rises in temperature (above 215°C) the stationary concentration of $K_3(MnO_4)_2$ decreases and one cannot detect it. Apparently, in the experiments of Herbstein and Weissman (*1*), precisely this factor, together with use of photo recording, led them to deny the existence of $K_3(MnO_4)_2$ at $KMnO_4$ thermal decomposition temperatures.

References

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FIG. 1. High-temperature X-ray diagrams characterizing changes in the phase composition of a $KMnO_4$ specimen in the process of thermal decomposition: (a) immediately after the $KMnO_4$ specimen reaches a temperature of 215°C; (b)–(g) after 11, 18, 28, 45, 52, and 59 min, respectively.