Preparation and Characterisation of the Compounds Sodium Tetraoxoniobate(V) Na_3NbO_4 and Sodium Tetraoxotantalate(V) Na_3TaO_4

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The preparation is described of two forms of the ternary oxide Na_3TaO_4 which are analogous to cubic and monoclinic forms of the compound Na_3NbO_4. A third orthorhombic form of each compound has been prepared by the reaction of sodium oxide with the transition metal under controlled conditions. The cubic form of the compound Na_3TaO_4 has been prepared as a single phase and the relationship of this phase to the monoclinic and orthorhombic forms is discussed.

THE ternary oxides Na_3NbO_4 and K_3NbO_4 are formed in the reactions of niobium pentoxide with liquid sodium and liquid potassium.[1,2] The corrosion of tantalum metal in liquid potassium yields the oxide K_3TaO_4[3] and in liquid sodium the oxide Na_3TaO_4.[4] We are currently interested in the corrosion of niobium and tantalum in liquid sodium, and as part of this study we have investigated the alkali-rich portion of the sodium oxide–niobium pentoxide and sodium oxide–tantalum pentoxide systems.

Sodium niobates and tantalates are generally prepared by the interaction of sodium carbonate or sodium nitrate with the appropriate pentoxide at high temperatures in an air or oxygen atmosphere.[5-9] In order that the preparations should resemble the conditions present in liquid metal environments, the reactions of both sodium oxide and sodium hydroxide with the pentoxides were investigated. Changing the alkali metal oxo-compound also enables different reaction temperatures to be used and frequently results in the formation of structurally different phases of the same compound.

The tetraoxoniobate(V) Na_3NbO_4 has been extensively studied;[9-11] much less information is available for the corresponding tantalate Na_3TaO_4.[11,12] The tetraoxoniobate(V) is known to exist in two allotropic modifications and we shall show that the tantalate also exists in two forms each of which is isostructural with the tetraoxoniobate forms. A third modification of the tetraoxoniobate(V) and tetraoxotantalate(V) has been prepared using sodium oxide reactions with the transition metal under special reaction conditions.

RESULTS AND DISCUSSION

Reactions of Sodium Carbonate and Nitrate with Niobium and Tantalum Pentoxides.—The ratios of starting materials, experimental conditions, and final products of reaction are shown in Table 1. All reactions were carried out in air. The *X*-ray powder diffraction patterns of Na_3NbO_4 were in complete agreement with those quoted by Bouillaud[13] for a mixture of two allotropic modifications, a face-centred cubic form (a = 4·606 Å) and a monoclinic form (a = 11·095, b = 12·993, and c = 5·730 Å with β = 108·9°). In accordance with the observation of Whiston and Smith[11] the compound Na_3TaO_4 was found to have an *X*-ray powder diffraction pattern closely resembling that of the mixture of the two allotropic modifications of Na_3NbO_4, and may therefore be considered a mixture of two allotropes isostructural with the corresponding niobate. Only one other compound type was observed in these reactions, the ABO_3 phase. There was no evidence for the existence of an $A_4B_2O_7$ phase as exists in the sodium oxide–vanadium pentoxide phase system, and as suggested[9] for the sodium oxide-niobium pentoxide system, at these reaction temperatures.

TABLE 1

Reactants	Temp. (°C)	Time	Products
$Na_2CO_3 + Nb_2O_5$	1000	2 days	$NaNbO_3$
$2Na_2CO_3 + Nb_2O_5$	850	1 day	$NaNbO_3 + Na_3NbO_4$
$3Na_2CO_3 + Nb_2O_5$	950	3 days	Na_3NbO_4
$Na_2CO_3 + Ta_2O_5$	1000	1 day	$NaTaO_3$
$2Na_2CO_3 + Ta_2O_5$	1000	2 days	$NaTaO_3 + Na_3TaO_4$
$3Na_2CO_3 + Ta_2O_5$	800	1 day	Na_3TaO_4
$6NaNO_3 + Nb_2O_5$	1000	12 h	Na_3NbO_4
$2NaNO_3 + Ta_2O_5$	1000	3 h	$NaTaO_3$
$6NaNO_3 + Ta_2O_5$	1000	1 h	Na_3TaO_4

Thermogravimetric analysis of the reactions involving sodium carbonate (3 mol) with the pentoxide (1 mol) showed a weight loss corresponding to the loss of carbon dioxide (3 mol) in each case. The reactions proceeded in a single stage starting at 400° (Nb_2O_5) and 500° (Ta_2O_5), the rate of reaction being greatest for the sodium carbonate–tantalum pentoxide reaction. The products of these reactions were always a mixture of the two crystal modifications of the tetraoxometallate(V). We were unable to obtain the cubic form of either Na_3TaO_4 or Na_3NbO_4 by prolonged heating at 900°; this is not in agreement with the work of Bouillaud[9] who prepared the cubic form of the tetraoxoniobate(V) by such a method. Prolonged heating at temperatures in excess

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[6] A. V. Lapitskii, *J. Gen. Chem.* (*U.S.S.R.*), 1946, **16**, 917.

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[8] M. W. Shafer and R. Roy, *J. Amer. Chem. Soc.*, 1959, **42**, 482.

[9] Y. Bouillaud, *Bull. Soc. chim. France*, 1965, 519.

[10] A. Reisman, F. Holtzberg, and E. Banks, *J. Amer. Chem. Soc.*, 1958, **80**, 37.

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[12] B. W. King, J. Schultz, E. A. Durbin, and W. H. Duckworth, U.S.A.E.C. Report B.M.I.-1106, 1956.

[13] Y. Bouillaud, *Bull. Soc. chim. France*, 1967, 3879.

of 1000° initiated the decomposition of the tetraoxometallate(v) to the trioxo form by the loss of sodium oxide.

$$Na_3TaO_4 \longrightarrow NaTaO_3 + Na_2O$$

Reactions of Sodium Hydroxide with the Pentoxides of Niobium and Tantalum.—The use of sodium hydroxide as a source of sodium oxide appears to stabilise the cubic form of both Na_3NbO_4 and Na_3TaO_4 since these compounds are obtained as single products of reaction when the temperature is held below 450°. Reactions carried out at temperatures above 800° gave both crystal forms of the tetraoxometallates. The cubic form of the compound Na_3NbO_4 may not be considered a high temperature form of the monoclinic modification as was implied [9] by the monoclinic to cubic conversion on prolonged heating at high temperatures.

TABLE 2

Reactants	Temp. (°C)	Product
$6NaOH + Nb_2O_5$	850	Na_3NbO_4 (cubic and monoclinic)
$7NaOH + Nb_2O_5$	450	Na_3NbO_4 (cubic) + NaOH
$8NaOH + Nb_2O_5$	450	Na_3NbO_4 (cubic) + NaOH
$9NaOH + Nb_2O_5$	450	Na_3NbO_4 (cubic) + NaOH
$10NaOH + Nb_2O_5$	450	Na_3NbO_4 (cubic) + NaOH
$6NaOH + Ta_2O_5$	850	Na_3TaO_4 (cubic and monoclinic)
$8NaOH + Ta_2O_5$	400	Na_3TaO_4 (cubic) + NaOH
$2NaOH + NaTaO_3$	800	Na_3TaO_4 (cubic and monoclinic)

Reactions carried out with greater than six mol of sodium hydroxide did not show any evidence for the formation of compounds [14,15] more alkali-rich than the tetraoxometallates.

Reaction of Sodium Oxide with Tantalum Pentoxide.—Sodium oxide reacts with tantalum pentoxide to form products identical with those obtained with sodium carbonate using comparable ratios of starting materials (Table 3). The compound Na_3TaO_4 was present as a mixture of the two allotropic modifications. The relative intensities of the diffraction patterns of the two forms were of the same order as was found for mixtures prepared using sodium carbonate, and the use of sodium oxide seemed in no way to stabilise one particular form of this compound. Reactions carried out under vacuum were observed to be extremely exothermic; reaction took place at 440° with the ejection of red hot fragments from the mixture. Associated with the reaction was a pressure change in the system which may be due to the loss of oxygen. Mixtures with more than **3** mol of sodium oxide lost sodium or sodium oxide which condensed in the cold part of the apparatus. An unknown phase (X) was present in the 4·84 : 1 mixture heated under vacuum; the identity of this phase will be discussed later in the paper.

TABLE 3

Reactants	Temp. (°C)	Atmosphere	Time	Products
$2{\cdot}6Na_2O + Ta_2O_5$	700	Argon	1 day	$NaTaO_3 + Na_3TaO_4$
$2{\cdot}6Na_2O + Ta_2O_5$	400	Vacuum	2 days	$NaTaO_3 + Na_3TaO_4$
$3{\cdot}0Na_2O + Ta_2O_5$	600	Vacuum	1 h	Na_3TaO_4
$4{\cdot}84Na_2O + Ta_2O_5$	600	Argon	1 day	$Na_3TaO_4 + Na_2O$
$4{\cdot}84Na_2O + Ta_2O_5$	600	Vacuum	1 day	$Na_3TaO_4 + Na + O_2 + X$

Reactions of Sodium Oxide with Niobium and Tantalum Metal.—Mixtures of sodium oxide and the transition metal were heated under vacuum at 550° in order to study the reaction

$$4Na_2O + M \longrightarrow Na_3MO_4 + 5Na$$

The sodium evolved in the reaction distilled from the mixture and condensed in the cold portion of the apparatus. Considerable difficulty was encountered when trying to establish equilibrium conditions in mixtures which were heated in pellet form. Mixtures in the form of well-mixed powders were therefore used, since these were found to attain equilibrium often without the need for reheating.

In accordance with the Phase Rule, only two solid phases were observed at equilibrium, namely the face-centred cubic form and sodium metal, and in no instance was the monoclinic phase produced in any reaction of sodium oxide with the transition metals. The *X*-ray powder diffraction patterns of products from reactions in which equilibrium was not attained were more complex, several phases being present. In some cases the equilibrium product, the cubic form, could be produced by prolonged heating of the mixture of phases at slightly higher temperatures. The unknown phase which had been observed in the $4{\cdot}84Na_2O + Ta_2O_5$ reaction under vacuum (Table 3) was prominent in the non-equilibrium products. A possible reason for the formation of this phase in these reactions was that the excess of sodium metal liberated in the reaction was not being removed entirely from the mixture. To examine this possibility sodium oxide and tantalum metal (in the molar ratio 4 : 1) were heated to 600° in an argon atmosphere over a period of one hour. The temperature of 600° was maintained for several minutes and the mixture cooled; the excess sodium was then removed by vacuum distillation at 300°. The *X*-ray powder diffraction pattern of the product was identical with that of the unknown phase. The corresponding niobate was prepared in a like manner except that the final distillation was carried out at 200°. The *X*-ray patterns of these compounds were tentatively indexed on the basis of an orthorhombic unit cell. Chemical analyses confirmed that these compounds may be regarded as being orthorhombic modifications of the tetraoxometallates.

Analysis of the Products.—Since the reactants were mixed in precisely known ratios, elemental analysis of products was unnecessary provided that the quantity of

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[14] V. I. Spitsyn and A. V. Lapitskii, *J. Appl. Chem.* (*U.S.S.R.*), 1953, **26**, 101.

[15] V. I. Spitsyn and N. N. Shavrova, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 1429.

any gases evolved was determined. Nevertheless, some routine analyses were carried out, and the results for the three forms of the tetraoxotantalate Na_3TaO_4, either as a single phase or as two phase mixtures, are shown in Table 4. The estimated error for the tantalum analyses (tannin method) is $\pm 4\%$. Some difficulty was encountered in these analyses due to the formation of the compound $NaTaO_3$ which was precipitated along with the pentoxide in some cases. Oxygen analyses were obtained by difference and are therefore subject to larger errors. Thermogravimetric analysis was used to provide the main method of analysis. The results (Table 5) show that sodium hydroxide reacts with the pentoxide and with the trioxotantalate(V) as soon as melting takes place. The reaction carried out at temperatures below 400° gave the cubic form of Na_3TaO_4 and showed the loss of exactly three mol of water. The formulation of the cubic and the monoclinic forms of the tetraoxometallates as Na_3MO_4 is therefore confirmed by the thermogravimetric analyses.

TABLE 4

	Cubic	Orthorhombic	Orthorhombic + cubic	Cubic + monoclinic	Calculated values for Na_3TaO_4	Na_5TaO_5	$NaTaO_3$
Na%	22·3	26·9	24·8	21·2	22·0	30·6	9·1
Ta%	55·4	55·8	53·4	58·0	57·6	48·1	71·8
O%	22·3	17·3	21·8	20·8	20·4	21·3	19·1

TABLE 5

Reactants	Reaction temp (°C)	Maximum temp (°C)	Products	CO_2 or H_2O evolved (mol)
$3Na_2CO_3 + Nb_2O_5$	400	1050	Na_3NbO_4 (cubic + monoclinic)	3·00
$3Na_2CO_3 + Ta_2O_5$	500	950	Na_3TaO_4 (cubic + monoclinic)	3·00
$6NaOH + Ta_2O_5$	320	850	Na_3TaO_4 (cubic + monoclinic)	3·00
$8NaOH + Ta_2O_5$	320	400	Na_3TaO_4 (cubic)	3·00
$2NaOH + NaTaO_3$	320	800	Na_3TaO_4 (cubic + monoclinic)	1·00
$6NaOH + Nb_2O_5$	320	850	Na_3NbO_4 (cubic + monoclinic)	3·00

TABLE 6

The *X*-ray powder diffraction pattern of cubic Na_3TaO_4

d_{obs}	d_{calc}	h	k	l	I_{obs}	I_{calc}
2·659	2·666	1	1	1	70	69
2·307	2·309	2	0	0	100	100
1·631	1·633	2	2	0	60	61
1·392	1·392	3	1	1	30	31
1·333	1·333	2	2	2	15	17
1·155	1·154	4	0	0	10	9
1·059	1·059	3	3	1	15	14
1·032	1·032	4	2	0	20	26
0·943	0·942	4	2	2	20	19
0·889	0·889	5	1	1	10	8

TABLE 7

The *X*-ray powder diffraction pattern of monoclinic Na_3TaO_4

d_{obs}	d_{calc}	I	h	k	l	d_{obs}	d_{calc}	I	h	k	l
8·06	8·12	40	1	1	0	2·703	2·702	35	0	0	2
6·44	6·44	35	0	2	0	2·616	2·615	40	4	0	0
5·38	5·40	100	0	0	1	2·585	2·593	7	3	0	$\bar{2}$
5·14	5·15	25	1	1	$\bar{1}$	2·515	2·517	15	3	1	1
4·14	4·14	35	0	2	1	2·495	2·492	4	0	2	2
4·06	4·06	50	2	2	0	2·308	2·308	60	4	3	1
3·98	3·97	40	1	3	0	2·128	2·129	15	2	0	2
3·75	3·74	45	2	2	$\bar{1}$	2·097	2·096	4	4	0	$\bar{1}$
3·42	3·41	15	1	3	$\bar{1}$	1·994	1·996	15	0	6	1
3·39	3·39	15	3	1	$\bar{1}$	1·793	1·793	20	2	6	1
3·36	3·36	25	3	1	0	1·782	1·784	40	0	1	3
3·03	3·02	20	1	3	1	1·650	1·649	25	4	3	$\bar{3}$
2·906	2·906	20	2	2	1	1·647	1·647	15	3	6	1
2·793	2·788	15	1	1	$\bar{2}$	1·629	1·630	20	1	2	3
2·754	2·767	50	0	4	1	1·626	1·625	20	4	5	1
2·747	2·747	50	2	1	$\bar{2}$	1·609	1·609	35	3	4	2

X-Ray Powder Diffraction Studies.—The indexed *X*-ray powder diffraction patterns of the cubic, monoclinic, and orthorhombic forms of Na_3TaO_4, and the orthorhombic form of Na_3NbO_4 are shown in Tables 6, 7, 8, and 9; the cell constants are given in Table 10. Approximate lattice parameters for the monoclinic form of Na_3TaO_4 were calculated by assigning the Miller indices of the first twenty diffraction lines of the niobate to the lines of the tantalate. Accurate parameters were then derived using a least squares refinement program[16] for the complete powder pattern. The orthorhombic phases were indexed using the computer program INDEX[17] adapted for use with the KDF9 computer.

TABLE 8

The *X*-ray powder diffraction pattern of orthorhombic Na_3TaO_4

d_{obs}	d_{calc}	I	h	k	l	d_{obs}	d_{calc}	I	h	k	l
5·18	5·18	100	2	1	1	2·174	2·178	5	6	2	0
5·12	5·11	30	1	2	1	2·031	2·035	10	1	5	3
4·79	4·80	35	0	0	2	1·995	1·998	10	5	2	3
4·51	4·52	100	0	1	2	1·967	1·970	10	3	6	1
4·15	4·15	10	3	0	1	1·937	1·940	10	4	5	2
4·06	4·06	80	0	3	1	1·859	1·858	20	7	2	1
3·50	3·50	10	2	3	1	1·823	1·826	5	7	0	2
3·15	3·16	35	4	1	1	1·806	1·806	8	7	3	0
3·09	3·09	5	1	4	1	1·791	1·790	7	0	5	4
3·01	3·02	10	2	4	0	1·780	1·781	3	0	7	2
2·959	2·959	40	2	3	2	1·768	1·768	8	4	5	3
2·728	2·735	25	4	3	0	1·742	1·741	3	3	7	1
2·715	2·713	40	3	4	0	1·729	1·727	5	8	0	0
2·677	2·669	40	3	3	2	1·699	1·700	15	4	4	4
2·561	2·559	30	1	3	3	1·674	1·676	10	7	4	1
2·474	2·470	5	5	2	1	1·649	1·650	5	5	5	3
2·420	2·422	5	2	5	1	1·632	1·633	5	6	4	3
2·400	2·402	5	0	0	4	1·600	1·601	5	2	7	3
2·360	2·362	10	3	4	2	1·570	1·572	7	4	3	5
2·351	2·351	25	5	3	0	1·517	1·517	7	8	4	1
2·317	2·317	5	0	4	3	1·479	1·479	10	9	2	1
2·271	2·270	40	6	1	0	1·445	1·445	7	0	4	6
2·214	2·217	30	4	2	3	1·433	1·433	10	3	3	6

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[16] Program PARAM, *X*-ray '63 Series of Crystallographic Programs.

[17] J. B. Goebel and A. S. Wilson, U.S.A.E.C. Report No. BNWL-22, 1965.

Several possible solutions were obtained all of which gave reliable mean deviations of $\sin^2 \theta$ values. The chosen solution was considered to have the most consistent set of calculated $\sin^2 \theta$ values and the smallest unit cell. The lattice parameters were again refined by a least-squares program.

TABLE 9

The X-ray powder diffraction pattern of orthorhombic Na_3NbO_4

d_{obs}	d_{calc}	I	h	k	l	d_{obs}	d_{calc}	I	h	k	l
5·17	5·17	95	2	1	1	2·034	2·031	5	1	5	3
5·12	5·11	15	1	2	1	1·995	1·994	8	5	2	3
4·79	4·79	20	0	0	2	1·966	1·968	10	3	6	1
4·50	4·50	100	0	1	2	1·935	1·937	7	4	5	2
4·14	4·15	5	3	0	1	1·856	1·856	30	7	2	1
4·05	4·05	100	0	3	1	1·823	1·824	5	7	0	2
3·49	3·49	10	2	3	1	1·806	1·805	10	7	3	0
3·15	3·16	30	4	1	1	1·789	1·786	7	0	5	4
3·09	3·09	3	1	4	1	1·780	1·779	3	0	7	2
3·00	3·02	5	2	4	0	1·767	1·765	10	4	5	3
2·954	2·954	25	2	3	2	1·740	1·739	3	3	7	1
2·721	2·732	25	4	3	0	1·728	1·726	5	8	0	0
2·711	2·710	45	3	4	0	1·697	1·697	20	4	4	4
2·674	2·665	45	3	3	2	1·673	1·674	15	7	4	1
2·555	2·554	55	1	3	3	1·649	1·648	5	5	5	3
2·469	2·467	3	5	2	1	1·631	1·631	5	6	4	3
2·419	2·419	5	2	5	1	1·600	1·598	10	2	7	3
2·399	2·395	5	0	0	4	1·570	1·569	10	4	3	5
2·357	2·359	10	3	4	2	1·516	1·515	5	8	4	1
2·348	2·349	30	5	3	0	1·478	1·478	7	9	2	1
2·270	2·268	55	6	1	0	1·443	1·441	10	0	4	6
2·213	2·213	40	4	2	3	1·432	1·429	10	3	3	6
2·172	2·176	5	6	2	0						

TABLE 10

Compound	Structure type	a (Å)	b (Å)	c (Å)	β
Na_3NbO_4 *	Cubic	4·606			
Na_3NbO_4 *	Monoclinic	11·095	12·993	5·730	108·9°
Na_3NbO_4	Orthorhombic	13·806	13·411	9·579	
Na_3TaO_4	Cubic	4·616			
Na_3TaO_4	Monoclinic	11·088	12·885	5·730	109·4°
Na_3TaO_4	Orthorhombic	13·818	13·426	9·608	

* Values obtained by Y. Bouillaud, *Bull. Soc. chim. France*, 1967, 3879.

Good agreement between observed and calculated line intensities was obtained from structure factor calculations based on the following atomic positions in the cubic form of the compound Na_3TaO_4; Ta (0, 0, 0), Na ($\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0; 0, $\frac{1}{2}$, $\frac{1}{2}$), oxygen ($\frac{1}{2}$, 0, 0; 0, $\frac{1}{2}$, 0; 0, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The structure is based on TaO_6 octahedra sharing corners with the sodium atoms in octahedral sites at the face-centre positions of the unit cell. In these compounds the oxide Ta_2O_5 may be considered[18] as the stable oxide being composed of octahedra distorted by edge-sharing. As the content of the structurally labile oxide (in this case sodium oxide) increases, the amount of edge-sharing should decrease at the expense of more corner-sharing. The compound Na_3TaO_4 represents the maximum content of sodium oxide that can exist with the oxide Ta_2O_5, and shows complete corner-sharing of the octahedra in the cubic phase.

At present, the X-ray powder data for the other forms of the tetraoxometallates is not sufficient to allow accurate information on atomic positions to be derived.

The Inter-relationship of the Three Forms of the Tetraoxometallates(V).—Our investigations do not support the monoclinic to cubic conversion[9] by prolonged heating of Na_3NbO_4 at high temperatures. The cubic phase may only be prepared as a single phase in reactions carried out at temperatures below 550°. Samples of the cubic form of Na_3TaO_4 when heated under helium in a high-temperature diffractometer remain unchanged at temperatures up to 600° but above this temperature diffraction lines attributable to the monoclinic phase become visible. Complete transformation of the cubic phase to the monoclinic phase is not possible by this means, though the orthorhombic phase may be transferred to a mixture of the cubic and monoclinic phases at 700°. Prolonged heating at temperatures above 1000° leads to the formation of the trioxo-form by loss of sodium oxide. The interconversion of the tetraoxometallates may therefore be a function not only of temperature but also of very small changes in stoicheiometry caused by the loss of sodium oxide. This loss is not an abrupt reaction; it proceeds very slowly at the lower temperatures, and is only readily observed at the higher temperatures. This study would therefore indicate that the orthorhombic phase is the alkali-rich compound, the cubic phase the stoicheiometric compound and the monoclinic phase the slightly deficient phase.

EXPERIMENTAL

The alkali metal nitrate, carbonate, and hydroxide were all of AnalaR grade. The purity of the transition metals and compounds was Nb_2O_5 99·99%, Ta_2O_5 99·9%, Nb 99·0%, Ta 99·5%. All reagents were dried to constant weight and stored in a dry argon atmosphere.

Sodium oxide was prepared by the reaction of sodium nitrate with excess liquid sodium at 230° in an alumina crucible. Excess sodium was removed by vacuum distillation at 300°. Using the liquid sodium at 230°, the nitrate reacted immediately on contact with the liquid metal. The presence of unreacted nitrate in any quantity during the distillation stage can result in **violent explosions**, and must be avoided. This method for the preparation of sodium oxide is to be preferred to that given by Brauer[19] which frequently results in violent explosions.

Preparation of Samples.—The reactions of sodium carbonate and sodium nitrate with the pentoxides were carried out with mixtures compressed into pellet form. Mixtures were heated in platinum or nickel crucibles in an electric furnace. Sodium hydroxide reactions were carried out with well-mixed powders in platinum crucibles. Mixtures with sodium oxide were prepared in an argon filled dry box, placed in nickel crucibles and loaded into silica glass tubes fitted with a tap so that the tube could be attached to the vacuum frame without exposing the mixture to the atmosphere. Thermogravimetric analyses were carried out using an Oertling single pan electronic balance; the sample was contained in a platinum crucible suspended from the balance by a silica thread. Heating rates variable between

[18] A. Reisman, *J. Phys. Chem.*, 1962, **66**, 15.

[19] G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' vol. I, Academic Press, New York, 1963, p. 975.

7° min^{-1} and 35° min^{-1} were provided by means of a temperature controller operating a 1 kW electric furnace.

All the X-ray data were collected on a Philips powder diffractometer using Cu-K_α radiation. Accurate peak position measurements were taken at a scan rate of $\frac{1}{8}$° 2θ per minute giving an estimated accuracy of ±0·005° 2θ. The theoretical values of the interplanar spacings shown in Table 6 were computed from the unit cell dimensions by the program D.SPAC.[20] modified for use with the KDF9 computer. Niobium and tantalum analyses were obtained by precipitation of the metals as the tannin complex, followed by ignition to constant weight as the pentoxide. Sodium was estimated using flame photometry.

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[20] M. E. Pippy, N.R.C. Crystallographic Program No. NRC-21, 1968.