Reactions of Tellurium Oxides with Alkali-metal Oxides and Hydroxides

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The double oxides Na_2TeO_4, K_2TeO_4, K_2TeO_3, and the triple oxides $Na_4Te_2O_7$ and $K_4Te_2O_7$ have been prepared by solid-state reactions of TeO_3 and $TeO_3{\cdot}H_2O$ with M_2O and $M[OH]$ (M = Na or K) and have been characterised by their *X*-ray diffraction patterns. The transformations and structures of the products obtained are discussed.

TELLURIUM differs from the other elements of Group 6B in its tendency to form mixed oxides with metallic elements. These compounds have typically ionic crystalline structures in which tellurium is present in its VI and/or IV oxidation states.[1,2] Relatively few studies have been carried out on the mixed anhydrous oxides of tellurium and alkali metals obtained by solid-state reactions.[3-5] The methods of synthesis used in this study avoid high temperatures or pressures and permit polycrystalline compounds to be obtained which are normally pure and from which it is hoped to produce single crystals, to enable a complete structural characterisation to be achieved. The solid phases obtained which correspond to the mixed oxides of tellurium-(VI) and -(IV) have not previously been described in the literature.

In previous studies, ' tellurates-(VI) and -(IV) ' were prepared in good yield by other synthetic methods from orthotelluric acid, H_6TeO_6, and alkali-metal hydroxides. These preliminary results allowed the prediction of the experimental conditions and processes described in this paper.[6] Thus the solid-state reactions have been studied to characterise the stable compounds in the M_2O (M = Na or K)–TeO_3–TeO_2 ternary system. The reactions of $TeO_3{\cdot}H_2O$ (usually called metatelluric acid) with sodium and potassium hydroxides at intermediate temperatures, and the reactions of TeO_3 with alkali-metal oxides in air at up to 700 °C, have also been studied and the reaction products have been identified. The synthesised compounds can be represented as solid phases of double oxides: $TeO_3{\cdot}M_2O$, $TeO_2{\cdot}M_2O$, and $Te_2O_5{\cdot}2M_2O$.

RESULTS AND DISCUSSION

The reaction characteristics and conditions together with the structures of the products obtained are given in Table 1.

Reactions of $TeO_3{\cdot}H_2O$.—The synthesis of Na_2TeO_4 and K_2TeO_4 from a mixture of $TeO_3{\cdot}H_2O(s)$ and $M[OH](s)$ (M = Na or K) in 1 : 2 molar ratio has been verified by heating to constant weight at 400 and 300 °C (for Na_2TeO_4 and K_2TeO_4 respectively) in air for 24 h. The preliminary operations were carried out in an inert atmosphere. The process [Table 1, reactions (i) and (ii)] can be represented by equation (1).

$$TeO_3{\cdot}H_2O(s) + 2\,M[OH](s) \longrightarrow M_2TeO_4(s) + 2\,H_2O(g) \qquad (1)$$

Quantitative chemical analysis carried out on the solid Na_2TeO_4 phase (whitish yellow, microcrystalline) and K_2TeO_4 (white, microcrystalline) and the parameters deduced for the unit cell are listed in Table 2. The systematic absences observed in the *X*-ray photographs indicated that Na_2TeO_4 belongs to the *P*222 or *Pmmm* space groups while that of K_2TeO_4 is *P*2/*m*.

TABLE 1

Reactions of tellurium oxides with alkali-metal oxides and hydroxides

Reaction	Reactants	Conditions	Product	System
(i)	$TeO_3{\cdot}H_2O$ + 2 Na[OH]	400 °C, in air	Na_2TeO_4	Orthorhombic
(ii)	$TeO_3{\cdot}H_2O$ + 2 K[OH]	300 °C, in air	K_2TeO_4	Monoclinic
(iii)	TeO_3 + Na_2O	650 °C, in air	$Na_4Te_2O_7$	Orthorhombic
(iv)	TeO_3 + K_2O	500 °C, in air	$K_4Te_2O_7$	Orthorhombic
(v)	TeO_3 + K_2O	700 °C, in air	K_2TeO_3	Tetragonal

Although some of these compounds with alkali metals have been known for a long time [7] (supposedly as derivatives of polymetatelluric acid, H_2TeO_4), the crystallographic data published are not reliable since the results of Patry,[7] who suggested isomorphism between $K_2[SO_4]$, K_2SeO_4, and K_2TeO_4, are not considered to be consistent. The four-co-ordination of tellurium in these compounds seems to be supported by spectroscopic data,[8] although in Na_2TeO_4 tellurium should be six-co-ordinate, as is customary for tellurium(VI) compounds. Mössbauer spectroscopic results [9] for Na_2TeO_4 are compatible with six-co-ordination for tellurium, and the existence of polymeric anions formed by $Te^{VI}O_6$ octahedrons joined at two vertices has been suggested by analogy with other alkali-metal oxo-derivatives whose structures are well known.[10]

However, no substantial differences were observed in the i.r. spectra of Na_2TeO_4 and K_2TeO_4 obtained in this

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study, and these compounds will be subjected to further research to clarify their structural nature.

TABLE 2

Analytical, crystallographic, and density results

Product	Analysis (%) *			Cell constant (Å)	Density (g cm^{-3})	
	TeO_3	M_2O	TeO_2		Crystallographic	Expt.
Na_2TeO_4	73.6 (73.9)	26.2 (26.1)		*a* 5.19 (4) *b* 6.32 (2) *c* 5.97 (2)	5.00	4.98
K_2TeO_4	64.8 (65.1)	34.7 (34.9)		*a* 5.47 (5) *b* 10.55 (2) *c* 4.62 (0) $\beta = 93.6°$	5.05	5.01
$Na_4Te_2O_7$	37.9 (38.2)	27.3 (27.0)	35.0 (34.8)	*a* 7.37 (6) *b* 5.50 (2) *c* 6.16 (3)	3.22	3.11
$K_4Te_2O_7$	33.2 (33.5)	35.8 (36.0)	30.2 (30.5)	*a* 7.23 (2) *b* 5.72 (1) *c* 6.92 (0)	3.04	2.97
K_2TeO_3		37.0 (37.1)	62.8 (62.9)	*a* 7.88 (2) *c* 7.45 (1)	3.64	3.46

* Calculated values are given in parentheses.

Reactions of TeO_3.—The reactions of amorphous tellurium trioxide with sodium and potassium oxides give solid products containing Te^{IV} and Te^{VI}. The preparation of compounds of stoicheiometry $M_4Te_2O_7$ has been carried out using a method similar to that previously described, but by heating in air at 650 and 500 °C (for sodium and potassium derivatives respectively) mixtures of TeO_3(s) and M_2O(s) in 1 : 1 molar proportions [Table 1, reactions (iii) and (iv)]. The process can be represented by equation (2).

$$2TeO_3(s) + 2M_2O(s) \longrightarrow M_4Te_2O_7(s) + 0.5\ O_2(g) \qquad (2)$$

The chemical analysis of $Na_4Te_2O_7$ (whitish, polycrystalline) and $K_4Te_2O_7$ (whitish yellow) and their unit-cell parameters are listed in Table 2. The possible space groups deduced for both compounds are *P*222 and *Pmmm* and *P*222, *Pmm*2, and *Pmmm* respectively. The densities determined by picnometry are in satisfactory agreement with those obtained crystallographically.

The existence of double oxides of tellurium of stoicheiometry $M^I_4Te_2O_7$ was demonstrated by Moret *et al.*[11] with the Li_2O–TeO_2 system. Only $Li_4Te_2O_7$, which has a triclinic structure, has been described. These compounds can be considered to be derivatives of ditellurium pentaoxide Te_2O_5 ($Te^{VI}O_3{\cdot}Te^{IV}O_2$) [12] and the corresponding alkali-metal oxide M_2O in a 1 : 2 molar ratio. The structural data reported here give further information on this new type of oxide. The characteristics of lithium, principally those related to its small size and high charge density,[5] could make the crystalline symmetry of $Li_4Te_2O_7$ very different from that of its sodium analogues. The sodium and potassium compounds possess similar unit-cell parameters and their differences can be attributed to the different sizes of the atoms.

When a mixture of TeO_3(s) and K_2O(s) is heated at 700 °C under the same conditions as those previously described [Table 1, reaction (v)] the compound K_2TeO_3 is obtained, while the reaction with sodium oxide at this temperature gives the double oxide $Na_4Te_2O_7$ together with another possible phase which could not be identified. The reaction with K_2O can be represented by equation (3).

$$TeO_3(s) + K_2O(s) \longrightarrow K_2TeO_3(s) + 0.5\ O_2(g) \qquad (3)$$

The analytical, crystallographic, and density data for K_2TeO_3 are in Table 2. The *c*/*a* quotient is 0.945 and the possible space group $P\bar{4}m2$.

The structural aspects of the double oxides of Te^{IV} with alkali metals have been little studied with the exception of Li_2TeO_3,[13] which has orthorhombic symmetry, space group *P*222, and parameters $a = 8.79$, $b = 10.52$, and $c = 7.10$ Å; its structure is probably of the same type as Li_2SeO_3. However, these results are not in agreement with those obtained by Moret *et al.*[14] for Li_2TeO_3 synthesised by solid-state reaction, which had monoclinic symmetry with cell parameters $a = 5.064$, $b = 9.540$, $c = 13.630$ Å, and $\beta = 95.35°$. The tellurites Na_2TeO_3 and K_2TeO_3 have been known for a long time and their respective *d* values are found in the A.S.T.M. card index, but neither their structures nor their unit-cell parameters have been determined. The *d* values obtained in this study for K_2TeO_3 do not coincide with those mentioned in the A.S.T.M. index, and so must relate to a different solid phase. The rubidium and caesium tellurites have also been described [15] although their crystallographic parameters have not been published. The cause of these inaccuracies lies in the difficult and laborious crystallisation of the products obtained by solid-state reactions or in solution.

An interesting structural variation can be observed in

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the potassium compounds studied, where there is a progressive increase in crystal symmetry: K_2TeO_4 (monoclinic) $\longrightarrow$ $K_4Te_2O_7$ (orthorhombic) $\longrightarrow$ K_2TeO_3 (tetragonal). A cubic modification of K_2TeO_3 or a non-stoicheiometric derivative of this compound is thought to exist and the preparation of this material is being studied.

EXPERIMENTAL

Reagents and Techniques —The compound $TeO_3{\cdot}H_2O$ was obtained by thermal decomposition of H_6TeO_6 (AnalaR, B.D.H.) to constant weight at 200 °C. The solid product is amorphous to *X*-rays and was characterised by the usual techniques of chemical anslysis[16] (Found: Te, 65.8. Calc.: Te, 65.9%) and thermal analysis (Found: weight loss, 15.7. Calc.: 15.8%). Tellurium trioxide, a yellowish amorphous solid, was prepared by complete dehydration of H_6TeO_6 by heating at 300 °C. Alkaline–metal hydroxides were supplied by Scharlau p.a.

The *X*-ray diffraction patterns were obtained using a Philips PW-1310 generator equipped with a chart recorder and cylindrical cameras of 114.6-mm internal diameter. Nickel-filtered Cu-K_α radiation was used. The patterns are available as Supplementary Publication No. SUP 22252 (6 pp.).*

The densities were determined by solid picnometric methods, using CCl_4 as the dispersant liquid.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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