tion.) Since the steady state established in diffusion or conductance is the result of a complicated interplay between competing forces, the resultant concentration dependence of these properties can be very different from the pattern typical of small strong electrolytes. To treat the conductance it would be necessary to compute the retarding force due to ion atmosphere lag and relaxation, an effect which does not alter the diffusion coefficient because all ions move with the same mean velocity. It is anticipated that the asymmetry of the ion atmosphere plays a relatively larger role in relaxation phenomena, which themselves result from atmosphere asymmetry, than in electrophoretic phenomena which result from the bulk motion of the entire atmosphere. The corresponding problems for polyelectrolytes are still more complex.

It would be of great interest to construct well defined models of polyions by synthesizing electrolytes with small numbers of charges distributed in some known manner on the molecular skeleton. Triply charged molecules with dimensions of the order of magnitude of those of the bolaform electrolytes considered herein would be a further step in bridging the gap between small electrolytes and polyelectrolytes. The study of such model compounds would undoubtedly contribute to the construction of a more definitive theory of polyelectrolyte solutions.

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO., INC.]

Preparation and Structure of the Strontium and Barium Tantalates $Sr_3TaO_{5.5}$ and $Ba_3TaO_{5.5}$

BY LOTHAR H. BRIXNER

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$Sr_3TaO_{5.5}$ and $Ba_3TaO_{5.5}$ have been prepared by the reaction of Ta_2O_5 with equivalent amounts of the corresponding carbonates at 1100° in oxygen. The compounds crystallize in the face centered cubic structure of $(NH_4)_3FeF_6$ with the space group, O_h^5. Four molecules constitute the unit cell with a lattice constant of 8.34 Å. for $Sr_3TaO_{5.5}$ and 8.69 Å. for $Ba_3TaO_{5.5}$. The pycnometric densities of 5.935 g. cc.$^{-1}$ and 6.798 g. cc.$^{-1}$ are in good agreement with the X-ray densities of 6.088 g. cc.$^{-1}$ and 6.906 g. cc.$^{-1}$, respectively. The dielectric constant of $Sr_3TaO_{5.5}$ is 14.3, and that of $Ba_3TaO_{5.5}$ is 13.18.

Introduction

Pauling[1] was the first to determine the structure of $(NH_4)_3FeF_6$, which is common to a series of compounds of the A_3BX_6-type. Between the straight complex fluorides, such as $(NH_4)_3FeF_6$, and the ternary oxides such as A_3BO_6, $(NH_4)_3MoO_3F_3$ constitutes an intermediate link, which also was investigated by Pauling earlier.[1] In 1951, Steward and Rooksby[2] found a series of tungstates, such as di-barium mono-calcium hexa-oxo-tungstate, which also belong to this class; and Ruedorff[3] characterized Ba_3UO_6 as another member of this series.

A fully-coördinated tantalate of the same type can only be expected when one of the cationic alkaline earth ions is replaced by a trivalent rare earth ion, such as trivalent lanthanum. Therefore, the compounds Sr_2LaTaO_6 with an $a_0 = 8.57$ Å. and Ba_2LaTaO_6 with an $a_0 = 8.62$ Å. were first prepared. However, when Ta_2O_5 was treated with $BaCO_3$ or $SrCO_3$ alone in a mole ratio 1:3, the X-ray pattern of the resulting compound could also be completely indexed according to the $(NH_4)_3FeF_6$ structure. This behavior can only be interpreted if one assumes an anion deficient structure for $Sr_3TaO_{5.5}$ and $Ba_3TaO_{5.5}$, similar to $SrTiO_{2.5}$, which Ward[4] recently found to crystallize in the perovskite structure of $SrTiO_3$.

Experimental

The new anion deficient strontium and barium tantalates are obtained readily by treating strontium or barium carbonate with Ta_2O_5 according to the equation

$$6MeCO_3 + Ta_2O_5 = 2Me_3TaO_{5.5} + 6CO_2 (Me = Sr, Ba)$$

This mixture is presintered at 800° for one hour in air and then ball-milled in a mechanical agate ball mill to ensure a homogeneous reaction mixture. The second firing takes place at 1100° in oxygen, using a platinum boat as a container. If amounts of 10–20 g. are processed, the evolution of CO_2 usually is complete after two hours, as is evident from the results in Table I.

TABLE I

CO_2 EVOLUTION DURING A 2-HR. FIRING PERIOD AT 1100° IN O_2

Compound	CO_2 calcd., g.	CO_2 given off, g.
$Sr_3TaO_{5.5}$	3.582	3.590
$Ba_3TaO_{5.5}$	2.985	2.979

The CO_2-free compounds were again ball milled, pressed into pellets under 40,000 p.s.i. and finally fired at 1200° for 1–2 hours. The strontium compound is white, while the barium compound is slightly yellow to pink.

Chemical Analysis.—The separation of strontium and tantalum was first attempted by dissolving the compound in molten $K_2S_2O_7$, precipitating $SrSO_4$ by diluting the melt in water, while tantalum was kept in solution with ammonium oxalate. The results are erratic because varying quantities of tantalum were precipitated with the strontium. Successful separation was effected by chlorinating the compounds with phosgene at 600° and leaching out the tantalum chloride with absolute alcohol. The alkaline earths were determined as sulfates; the tantalum, by precipitating in freshly filtered ammoniacal solution and igniting in air to the pentoxide.

The analytical results were as follows: $Sr_3TaO_{5.5}$, found, 34.97% Ta, 48.49% Sr, Sr:Ta = 1:2.97; calcd., 34.01% Ta, 49.44% Sr, Sr:Ta = 1:3.00. For $Ba_3TaO_{5.5}$, found, 26.49% Ta, 60.63% Ba, Ba:Ta = 1:3.01; calcd., 26.56% Ta, 60.51% Ba, Ba:Ta = 1:3.00.

Dielectric Constant.—For the measurement of the dielectric constant a pellet, 1.25 cm. in diameter, 2 mm. thick, was pressed at 40,000 p.s.i. and silver-coated on both sides. The measurement was carried out at 200 kilocycles. The dielectric constant of $Sr_3TaO_{5.5}$ was found to be 14.3, and that of $Ba_3TaO_{5.5}$, 13.18.

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(1) L. Pauling, THIS JOURNAL, **46**, 2738 (1924).

(2) Rooksby and Steward, *Acta Cryst.*, **4**, 503 (1951).

(3) W. Ruedorff, *Z. Naturforsch.*, **9b**, Heft 8, 568 (1954).

(4) M. Kestigian, J. G. Dickinson and R. Ward, THIS JOURNAL, **79**, 5598 (1957).

TABLE II

hkl	d_0	d_c	I_0[a]	d_0	I_0 for Ba_2CaWO_6[b]
111	4.82	4.815	m^+	4.84	22
200	4.17	4.170	m^-	4.20	1
220	2.948	2.949	s^+	2.97	100
311	2.516	2.514	m	2.53	9
222	2.403	2.408	w	2.42	4
400	2.082	2.085	s^-	2.10	30
331	1.913	1.913	m^-	1.925	4
420	1.864	1.865	m		..
422	1.702	1.702	s	1.713	37
333	1.604	1.605	m	1.615	4
440	1.474	1.474	m^+	1.483	15
531	1.411	1.410	m^-	1.418	4
442	1.391	1.390	w		..
620	1.320	1.319	m^+	1.327	15
533	1.272	1.272	w^-	1.279	1
622	1.258	1.257	w^-	1.265	1
444	1.204	1.204	w	1.211	6
711	1.168	1.168	w	1.175	3
640	1.157	1.157	w^-		..
642	1.116	1.115	m^+	1.121	22

[a] s = strong, m = moderate, w = weak. [b] Data taken from A.S.T.M. card 6-0400.

X-Ray Analysis.—The compounds were investigated in powder form in hermetically sealed Lindemann glass capillaries in order to avoid any hydrolysis. Copper radiation ($\lambda = 1.5418$) was used, filtering the β-radiation with a nickel filter. In Table II are summarized the observed and calculated interplanar spacings as well as the observed[2] intensities of Ba_2CaWO_6 for comparison. The lattice constant for $Sr_3TaO_{5.5}$ of 8.34 Å. is very close to that for Ba_2CaWO_6 of 8.39 Å. Steward and Rooksby[2] found that this compound belongs to the cubic $(NH_4)_3FeF_6$-type which crystallizes in the space group O_h^5. The observed diffraction lines have either all odd or all even indices, indicating a face-centered cubic structure. Since the patterns of $Sr_3TaO_{5.5}$ and Ba_2CaWO_6 are essentially identical and since the concordance of the intensities is good, it can be stated that $Sr_3TaO_{5.5}$ crystallizes in the same structure, that is, in the $(NH_4)_3FeF_6$-type. In Table III are given the observed and calculated interplanar spacings for the compounds Ba_2LaTaO_6 with a_0 = 8.62 Å., Sr_2LaTaO_6 with a_0 = 8.27 Å. and $Ba_3TaO_{5.5}$ with a_0 = 8.69 Å.

TABLE III

OBSERVED AND CALCULATED INTERPLANAR SPACINGS OF

	$Ba_3TaO_{5.5}$			Ba_2LaTaO_6			Sr_2LaTaO_6		
hkl	d_0	d_c	I_0	d_0	d_c	I_0	d_0	d_c	I_0
111	5.01	5.017	m	4.98	4.97	w	4.77	4.77	m
200	4.34	4.345	w	4.32	4.31	w	4.13	4.13	m
220	3.07	3.072	s^+	3.06	3.045	s^+	2.92	2.921	s^+
311	2.618	2.620	w^-	2.60	2.599	w^-	2.49	2.492	m^-
222		2.509		2.50	2.485	w^-	2.40	2.385	w^-
400	2.170	2.172	s^-	2.16	2.155	s^-	2.06	2.062	s^-
331	1.992	1.994	m	1.97	1.977	w^-	1.90	1.896	w
420		1.943		1.93	1.927	w^-	1.86	1.849	w
422	1.772	1.774	s	1.76	1.760	s	1.69	1.689	s
333	1.671	1.672	m	1.66	1.658	w^-	1.59	1.590	m
440	1.534	1.536	m^+	1.53	1.522	m^+	1.46	1.461	m^+
531	1.468	1.469	w	1.45	1.457	w^-	1.39	1.398	w
442		1.448			1.436		1.38	1.378	w^-
620	1.373	1.374	m^+	1.36	1.361	m^+	1.31	1.306	w
533	1.323	1.325	w		1.313		1.26	1.261	w^-
622		1.310			1.300			1.247	
444	1.253	1.254	w	1.25	1.243	w	1.19	1.192	w^-
711	1.217	1.217	$w^=$		1.207			1.158	
640		1.205			1.195			1.136	
642		1.160	m	1.15	1.151	m^+		1.104	

Discussion

The reaction between stoichiometric amounts of Ta_2O_5 and $SrCO_3$ or $BaCO_3$ to form $Me_3TaO_{5.5}$ as a pure phase, indicates that, in the case of the $(NH_4)_3FeF_6$ structure, there might be a similar range of anion deficient structures as has been observed for the perovskites. In the case of tungsten and uranium, compounds like $Ba_3WO_{5.5}$ and $Ba_3UO_{5.5}$ can be postulated with the transition elements in the 5-valent oxidation state.

Since there are four molecules per cell, a total of two oxygens are missing in the unit cell of the compound $Sr_3TaO_{5.5}$. The question as to whether these vacancies are randomly distributed or located at definite lattice sites can only be answered by a more precise X-ray investigation.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Organic Disulfides as Initiators of Polymerization. Part II[1]

BY T. FERINGTON[2] AND A. V. TOBOLSKY

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The study of the compound tetramethylthiuram disulfide (TMTD) as an initiator of the polymerization of methyl methacrylate has been extended to 60 and 80°. The experimental points are fit by the equation $R'_i/(\text{cat.}) = 4.80 \times 10^{14} \exp(-31.6\ \text{kcal.}/RT)$. This equation falls in the same range as the similar expression for, *e.g.*, benzoyl peroxide, although the S–S bond is much stronger than the O–O bond. TMTD also has a retarding effect which was studied at 30° where the initiating effect does not appear. Retardation is due to radical attack on the TMTD molecule to produce an inhibiting TMTD radical residue. Evidence on the photoactivity of TMTD also was obtained. Various polar reagents were studied as to their effect on the rate of generation of radicals by TMTD but no pronounced change was found. A comparison with vulcanization data for TMTD indicates similar primary steps in vulcanization and polymerization by this compound. Tetramethylthiuram monosulfide (TMTM) was studied in the same way as TMTD at 70, 80, 90°. No retardation was found. The experimental points for initiation were fit by the equation $(R'_i/\text{cat.}) = 9.0 \times 10^{11} \exp(-29.4\ \text{kcal.}/RT)$. The energy of activation is very similar to that for TMTD. Experimental observations on the photoactivity of TMTM are given. Dipentamethylenethiuram tetrasulfide was found to have a purely retarding behavior with methyl methacrylate. Diphenyl disulfide, while much less active than TMTD, shows a very similar combination of initiating and retarding ability at 100°. A mechanism is presented which fits the above observations. Retardation is due to polysulfide radical species, $RS_x\cdot$ ($x > 1$) and initiation through the intermediate radical $RS\cdot$. In the case of thiuram compounds this latter is unstable and further decomposes to $CS_2 + (CH_3)N\cdot$. This mechanism is consistent with most of the observed data on thiuram vulcanization.

Introduction

In the previous publication the decomposition of the compound tetramethylthiuram disulfide (TMTD) was studied at 70° in the presence of the common vinyl monomers styrene and methyl

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[1] Part I is T. Ferington and A. V. Tobolsky, THIS JOURNAL, **77**, 4510 (1955).

[2] This article is based upon a dissertation submitted by Thomas Ferington in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.