tures, thus eliminating the mechanism of ring-chain equilibrium. Under normal circumstances (*i.e.*, water initiation), two simultaneous equilibria have to be accounted for, *i.e.*, the ring-chain equilibrium and the ring-large ring equilibrium. Since large rings are present only in relatively small concentrations, these may be neglected in studying the ring-chain system, and this actually was done (see Application I-a). Once M is known for this simplified system, it could be regarded as M_0 for the ring-large ring equilibrium.

Appendix 1

Just as in case I-a

$$P = \frac{M_0 - M}{X_0 - X}$$

where X_0 and X are related by the equation

$$X_0 = X(1 + K_3MP)$$

but for high values of P, by equation 16

$$K_3 = \frac{1}{M} \text{ or } K_3M = 1$$

therefore

$$X_0 \simeq X(1 + P) \simeq XP \text{ for } P \gg 1$$

substituting

$$\begin{aligned} P &= (M_0 - M)/(X_0 - X_0/P) \\ &= (M_0 - M)/X_0(1 - 1/P), \text{ yielding} \\ P &= (M_0 - M)/X_0 \text{ for } P \gg 1 \end{aligned}$$

PRINCETON, N. J.

[CONTRIBUTION FROM THE PRODUCTS RESEARCH DIVISION, ESSO RESEARCH AND ENGINEERING COMPANY AND THE DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

High Temperature X-Ray Study of Lead Halides and Oxyhalides[1a]

BY H. PAUL JULIEN[1b] AND ROBERT E. OGILVIE

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Several complexes of lead oxide, lead chloride and lead bromide were studied by X-ray diffraction over the temperature range 20 to 650°. Samples were heated in air in a high temperature furnace attached to a high angle diffractometer. $PbCl_2$ and $PbBr_2$ heated with PbO in air formed stable lead oxyhalides by irreversible reactions. Several new lines were observed in the X-ray diffraction patterns of PbClBr and $2PbO\cdot PbClBr$. Approximate temperatures of formation were determined for PbClBr, $PbO\cdot PbBr_2$, $2PbO\cdot PbBr_2$ and $2PbO\cdot PbClBr$. The "R" form of $PbO\cdot PbBr_2$ was shown to be the only stable variety of the four polymorphic forms reported for this compound. Anisotropic expansion was observed in $PbCl_2$ and PbClBr. Lattice constants were calculated from precise, room temperature X-ray data on three compounds: PbClBr: $a = 4.577$, $b = 7.811$, $c = 9.172$ Å.; $2PbO\cdot PbBr_2$: $a = 9.8$, $b = 12.2$, $c = 5.83$ Å.; $2PbO\cdot PbClBr$: $a = 9.7$, $b = 12.1$, $c = 5.87$ Å. Good agreement with published values was obtained. These results suggest that $2PbO\cdot PbX_2$, like PbO and PbX_2, has a layer structure, with a and b unit cell dimensions almost equal to the sum of the PbO and PbX_2 dimensions, and with the c dimension very nearly equal to that of PbO.

Introduction

Although a vast amount of literature is available on the chemical and physical properties of the lead halides and lead oxides, such information on the lead oxyhalides is less abundant. Moreover, data on the mixed halides (*e.g.*, lead chlorobromide) and on complexes of these mixed halides with the lead oxides are very scanty. This paper presents the results of a high temperature X-ray diffraction study of lead chlorobromide (PbClBr), trilead dioxychlorobromide ($2PbO\cdot PbClBr$), dilead oxydibromide ($PbO\cdot PbBr_2$) and trilead dioxydibromide ($2PbO\cdot PbBr_2$). This study permitted the direct observation of many chemical and physical changes occurring over the temperature range 20–650°.

Calingaert, Lamb and Meyer[1c] studied the lead chloride–lead bromide system by thorough X-ray diffraction analysis. They also investigated the system by thermal analysis, conductivity measurements and aqueous preparations in order to resolve the discrepancies in the earlier literature on the $PbCl_2$–$PbBr_2$ system. They concluded that a compound PbClBr exists which is stable at room temperature. However, no such solid-state compound formation was observed by Harrap and Heymann[2] in their viscosity and equivalent conductance measurements on this $PbCl_2$–$PbBr_2$ system.

A phase study of the lead oxide–lead bromide system by X-ray diffraction was carried out by Lamb and Niebylski,[3] who found published X-ray data only for the compound $PbO\cdot PbBr_2$. Their study showed these data to be in error. A later X-ray study 4 of the $PbBr_2$-rich region of the PbO–$PbBr_2$ system confirmed the existence of a $2PbO\cdot PbBr_2$ but revealed two other compounds rather than the $PbO\cdot PbBr_2$ reported by earlier workers. For the compound $2PbO\cdot PbBr_2$, the two available sets[5,6] of interplanar spacing values reveal several inconsistencies. The only X-ray data in the literature[5] on $2PbO\cdot PbClBr$ are not in good agreement with the two independent sets of data obtained in this work.

Experimental

The lead compounds being studied were heated in a high temperature furnace attached to a standard Norelco high

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[1a] Presented before the Division of Physical Chemistry, 135th national meeting of the American Chemical Society, Boston, Mass., April, 1959.

[1b] Bonded Abrasives Division, The Carborundum Company, Niagara Falls, N. Y.

[1c] G. Calingaert, F. W. Lamb and F. Meyer, THIS JOURNAL, **71**, 3709 (1949).

[2] B. S. Harrap and E. Heymann, *Trans. Faraday Soc.*, **51**, 259 (1955).

[3] F. W. Lamb and L. M. Niebylski, THIS JOURNAL, **75**, 511 (1953).

[4] P. T. Davies, E. V. Garner and B. D. Caddock, *Acta Cryst.*, **7**, 640 (1954).

[5] F. W. Lamb and L. M. Niebylski, *Anal. Chem.*, **23**, 1388 (1951).

[6] "X-Ray Diffraction Patterns of Lead Compounds," The Shell Petroleum Company Limited, Chester, England, 1954.

angle diffractometer. This furnace had a platinum winding and a maximum temperature of 1300°. Samples were contained in high purity alumina holders and heated in air. The reaction products were mounted on glass slides and examined on a General Electric diffractometer to obtain precise measurements for calculation of lattice parameters. With both instruments copper Kα radiation was used. Patterns were run from high angles to low, with a scanning speed of 2 degrees/minute.

X-Ray diffraction patterns were obtained over a range of temperatures for the simple compounds PbO (red), $PbBr_2$ and $PbCl_2$. Then a series of lead oxyhalides and mixed halides was studied. These included PbClBr, $PbO \cdot PbBr_2$, $2PbO \cdot PbBr_2$ and $2PbO \cdot PbClBr$. Maximum temperatures of observation were limited by melting point, compound formation and rate of vaporization. In all cases, the compounds had such high vapor pressures that the specimens would have been completely evaporated within a few hours at 700–800°. The geometry of the surfaces was changed to such an extent at 500° that the position of the lines was not reliable. However, in all cases the phases could be identified. Patterns were made at several intervals during both heating and cooling of the samples.

Over 100 X-ray patterns were made in this study. All were closely examined for compound formation or decomposition, phase transitions, solid state reactions and lattice distortions due to anisotropic expansion. The reversibility of any of these changes was determined on the cooling part of the cycle.

Results

1. **Irreversible Reactions.**—The most important conclusion from this work is the irreversibility of the chemical reactions involved in the formation of PbClBr and the various lead oxyhalides. The high melting points and large negative free energies of formation of many of these compounds strongly suggested that the reactions were irreversible. However, no definite proof was available.

This study showed conclusively that the complex lead compounds formed at high temperature but previously identified by X-ray diffraction analysis only at room temperature are the same compounds present at the high temperature. No chemical changes take place when the compounds are cooled to room temperature. Thus, the lead oxyhalides do *not* undergo phase transitions or revert to lead oxide and lead halide at temperatures below the temperature of formation.

2. **New Lines.**—Several new lines were observed in the room temperature X-ray diffraction patterns of PbClBr and $2PbO \cdot PbClBr$. Table I lists the interplanar spacing values observed for PbClBr, $2PbO \cdot PbClBr$, and $2PbO \cdot PbBr_2$, all at room temperature. Miller indices (*hkl*) and relative intensities (I/I_0) have been tabulated for each *d*-spacing. New assignments of indices were calculated for four *d*-values.

Only five interplanar spacing values have been published for PbClBr,[1] and these are in good agreement with the more complete data listed in Table I. The only literature values available for $2PbO \cdot PbClBr$[5] do not agree well either with the *d*-spacings reported in Table I or with data obtained in a companion study,[7] whereas the latter two independent sets of data are in excellent agreement. Values for $2PbO \cdot PbBr_2$ obtained in this work agree well with one[6] of the two sets of published data[5,6] on this compound.

Table I

Interplanar Spacing Values

(Copper Kα radiation) [a] Indicates new assignments.

PbClBr		2PbO·PbClBr			$2PbO \cdot PbBr_2$		
(*hkl*)	*d* (Å.)	(*hkl*)	*d* (Å.)	I/I_0	(*hkl*)	*d* (Å.)	I/I_0
(002)	4.62	(110)	7.69	m	(110)	7.69	m
(101)	4.07	(120)	5.15	m	(120)	5.21	mw
(012)	3.96	(200)	4.90	vw	(200)	4.89	w
(020)	3.88	(111)	4.67	vw	(111)	4.67	vw
(111)	3.63	(021)	4.21	w	(021)	4.25	vw
		(121)	3.86	ms	(121)	3.89	mw
(120)	2.995	(211)	3.57	ms	(211)	3.60	m
(112)		(131)	3.14	vs (2)	(131)	3.17	vs (3)
(022)		(230)	3.10	s	(230)	3.15	s
		(002)	2.938	s	(002)	2.947	s
(121)	2.829						
(103)	2.547	(320)	2.846	vs (1)	(320)	2.864	vs (1)
(113)	2.421	(301)			(301)		
(200)	2.285	(311)	2.769	m	(311)	2.786	s
(004)		(112)	2.673	vs (3)	(112)	2.720	vs (2)
		(240)	2.561	w	(240)	2.597	w
(032)	2.268	(321)	2.526	w	(321)	2.554	m
		(400)	2.434	vw	(400)	2.453	vw
		(241)[a]	2.342	vw	(241)[a]	2.378	w
		(132)	2.252	vw	(132)	2.274	vw
		(340)	2.204	m	(340)	2.236	m
		(232)	2.125	ms	(232)	2.144	m
		(341)	2.043	w			
		(322)					
		(060)	2.004	w	(060)	2.038	w
		(431)[a]	1.959	vw			
		(242)[a]	1.920	m			

3. **Temperatures of Formation.**—In some cases it was possible to estimate the temperatures of formation of new compounds such as the oxyhalides. Table II indicates the approximate temperatures of formation of PbClBr, $PbO \cdot PbBr_2$, $2PbO \cdot PbBr_2$ and $2PbO \cdot PbClBr$, as a result of the heating in air of stoichiometric mixtures of α-PbO, β-PbO, $PbCl_2$ and $PbBr_2$. In all cases cooling to room temperature did not alter the composition of the high temperature compound.

Table II

Temperatures of Formation of Lead Chlorobromide and Lead Oxyhalides

Reactants	Products	Temp. of formation, °C.
$PbCl_2 + PbBr_2$	PbClBr	295
β-PbO + $PbBr_2$	$PbO \cdot PbBr_2$ (R form)	290
	$2PbO \cdot PbBr_2$	490
α-PbO + $PbBr_2$	$PbO \cdot PbBr_2$	360
	$2PbO \cdot PbBr_2$	500
2β-PbO + $PbBr_2$	$2PbO \cdot PbBr_2$	390
2α-PbO + $PbBr_2$	$2PbO \cdot PbBr_2$	375
2β-PbO + $^1/_2PbCl_2$ + $^1/_2PbBr_2$	$2PbO \cdot PbClBr$	355

4. **$PbO-PbBr_2$ Phases.**—The high temperature X-ray data on the $PbO-PbBr_2$ system obtained in this work partially confirm the phase diagram of Knowles.[8] However, these data do not support the conclusion that $PbO \cdot PbBr_2$ exists in four polymorphic forms, as reported by Lamb and Niebylski.[3] These authors also discuss the preferential production of one of the crystalline modifications, the R form, by low temperature solid-state reaction. From the X-ray patterns made in this study it can be concluded that *only* the R form is stable. It is doubtful that the other forms of $PbO \cdot PbBr_2$ are even metastable phases. It seems likely that the differences in the X-ray

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(7) Esso Research and Engineering Company, unpublished data.

(8) L. M. Knowles, *J. Chem. Phys.*, **19**, 1128 (1951).

data of Lamb and Niebylski for $PbO \cdot PbBr_2$ can be ascribed to water of hydration. A modified phase diagram for this system is mentioned in the more recent work of Davies, *et al.*[4]

5. Anisotropic Expansion.—The X-ray patterns in this high temperature study were carefully examined for evidence of anisotropic expansion of the crystal lattice, *i.e.*, non-uniform expansion along the crystal axes. The orthorhombic structure of the lead halides and oxyhalides is especially conducive to such anisotropic expansion.

This phenomenon was observed in both $PbCl_2$ and PbClBr. Each of several lines in these isomorphic compounds split into two lines at temperatures above 150° and then recombined upon cooling to room temperature. Table III reveals the splitting of the (200) and (004) line of $PbCl_2$ as a function of temperature. This table shows that the $PbCl_2$ crystal expands faster along the *c*-axis than along the *a*-axis. This result agrees with the *a*, *b*, *c* values for $PbCl_2$ and $PbBr_2$ listed in the next section: the difference between the *c* values is much larger than that for the *a* values.

TABLE III

ANISOTROPIC EXPANSION IN LEAD CHLORIDE

	d (Å.)				
Temp., °C.	20	87	180	258	386
(004) Line	2.29	2.30	2.31	2.32	2.34
(200) Line	2.29	2.30	2.30	2.30	2.31

6. Lattice Constants.—Lattice constants were calculated for PbClBr, $2PbO \cdot PbClBr$ and $2PbO \cdot PbBr_2$. The interplanar spacings *d* were obtained in the usual way[9] from 2θ values read directly from precise, room temperature X-ray patterns. Assignments of indices to the *d*-values were based on an assumed space group $P2_12_12_1$ (corresponding to an orthorhombic structure) and on previous assignments for the pure lead halides and oxyhalides. Assignments for PbClBr were made by interpolation in the values for $PbCl_2$ and $PbBr_2$. The indices assigned to $2PbO \cdot PbClBr$ were based on values for $2PbO \cdot PbCl_2$ and $2PbO \cdot PbBr_2$.

The lattice constants *a*, *b*, and *c* for these orthorhombic crystals were calculated using standard procedures. The values of the constants derived from these data agree very well with those in the literature and those obtained at the Esso Research and Engineering Company, as shown in Table IV.

TABLE IV

LATTICE CONSTANTS OF LEAD HALIDES AND TRILEAD DIOXYDIHALIDES

	Lattice constants (Å.)			
Compound	*a*	*b*	*c*	Ref.
β-PbO	5.489	4.755	5.891	10a
$PbCl_2$	4.535	7.623	9.045	10b
PbClBr	4.560	7.798	9.182	7
	4.562	7.795	9.198	1
	4.577	7.811	9.172	This work
$PbBr_2$	4.732	8.060	9.553	10c
$2PbO \cdot PbCl_2$	9.5	11.9	5.76	7
	9.5	11.9	5.77	6
$2PbO \cdot PbClBr$	9.7	11.9	5.76	7
	9.7	12.1	5.87	This work
$2PbO \cdot PbBr_2$	9.7	12.1	5.88	4
	9.7	12.1	5.88	6
	9.8	12.2	5.82	7
	9.8	12.2	5.83	This work

Lattice constants for the simple components and $2PbO \cdot PbCl_2$ are included for completeness.

The effect of incorporating PbO into the lead halide lattice is revealed clearly by a comparison of the lattice constants for β-PbO and the series of lead halides and trilead dioxydihalides. This comparison is given in Table IV. The values for PbClBr are much closer to $PbCl_2$ than to $PbBr_2$; the unit cell for lead bromide is substantially larger. However, incorporation of PbO leaves $2PbO \cdot PbClBr$ midway between $2PbO \cdot PbBr_2$ and $2PbO \cdot PbCl_2$ in unit cell dimensions. It is interesting to note that *a* and *b* for the trilead dioxydihalides are very nearly the sums of *a* and *b*, respectively, for β-PbO and lead halide, whereas the *c* value for the complex is very nearly that of β-PbO. Although the limited data do not permit a firm conclusion, these data and the known layer structures of β-PbO and PbX_2 suggest that the trilead dioxydihalides also have a layer structure, in which the PbO is incorporated into the horizontal planes of the lead halide lattice and in which the vertical dimension of the unit cell is that of PbO.

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(9) "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing," Nat. Bur. Std., Appl. Math. Series 10 (Washington, D. C.), 1950.

(10) ASTM X-Ray Powder Data File: (a) Card No. 5-0570; (b) Card No. 5-0416; (c) Card No. 5-0608.