Summary

1. Initial cyclization of heptylene-1 on chromium oxide catalysts is more rapid than that of heptane. The catalysts poison more rapidly.

2. Heptylene-1 in 15% concentration in heptane reduces the over-all conversion to toluene.

3. Methylcyclohexane is more rapidly dehydrogenated to toluene than heptane or heptylene-1 and does not poison the catalyst.

4. Ethylene strongly poisons chromium oxide catalysts by deposition of carbonaceous material on the surface, removable only by oxidation.

5. Simultaneous presence of hydrogen reduces and may eliminate the poisoning action of ethylene.

6. Analysis of the data indicates that dehydrogenation of the heptane is inhibited by heptylene and is the slow process in the whole sequence.

7. Aromatization is more sensitive to poisons than the paraffin dehydrogenation.

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The Crystal Structures of the Tetragonal Monoxides of Lead, Tin, Palladium, and Platinum

BY WALTER J. MOORE, JR.,* AND LINUS PAULING

The crystal structure of red plumbous oxide was first investigated by Dickinson and Friauf,[1] who found the tetragonal unit to have $a_0 = 3.99$ Å. and $c_0 = 5.01$ Å., and to contain 2Pb at $\frac{1}{2}0z$, $0\frac{1}{2}\bar{z}$, with $z = 0.24$, and 2O at 000, $\frac{1}{2}\frac{1}{2}0$. This is a very interesting layer structure, in which each oxygen layer is sandwiched between two lead layers. Subsequently Levi and Natta[2] reported this structure to be incorrect, and assigned to the oxygen atoms the atomic positions $0\frac{1}{2}v$, $\frac{1}{2}0\bar{v}$, with $v \backsimeq 0.76$. This corresponds to a distorted sodium chloride arrangement. A similar structure was reported by them for stannous oxide also. Both the Dickinson–Friauf structure and the Levi–Natta structure are described in detail in the "Strukturbericht."

In 1927 Zachariasen[3] reported that powder pictures of palladous oxide show it to be tetragonal, with $a_0 = 3.029 \pm 0.005$ Å. and $c_0 = 5.314 \pm 0.005$ Å. He concluded that the crystal is probably isomorphous with PbO and SnO, without deciding between the Dickinson–Friauf and Levi–Natta arrangements. It was then pointed out by Huggins[4] that neither of these arrangements provides the bond configuration expected for bivalent palladium, and the structure 2Pd at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, 2O at $\frac{1}{2}0\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$ was suggested and shown to be not incompatible with the reported data.

The present investigation was undertaken to resolve these discrepancies. We have verified the Dickinson–Friauf structure for plumbous oxide, have shown that stannous oxide has the same structure, and have found that palladous oxide is not isomorphous with these crystals, but has the structure suggested by Huggins. We have also found that platinous oxide has this same structure.

Experimental Methods and Results.—Red plumbous oxide was prepared by the action of hot 15 *N* potassium hydroxide solution on the hydroxide, and stannous oxide by boiling a suspension of the hydroxide to which a crystal of stannous chloride had been added.[5] Palladous oxide was prepared by the method of Shriner and Adams,[6] involving fusing palladous chloride and potassium nitrate, and platinous oxide by a similar method. Powder photographs of the substances were made with copper Kα radiation filtered through nickel, in a cylindrical camera with 5-cm. radius. Three films, one behind another, were exposed simultaneously, and the relative intensities of the powder lines were estimated by visual comparisons.

The tetragonal unit of plumbous oxide was found from our films to have $a_0 = 3.947 \pm$

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[1] R. G. Dickinson and J. B. Friauf, THIS JOURNAL, **46**, 2457 (1924).

[2] G. R. Levi and E. G. Natta, *Nuovo Cimento N. S.*, **3**, 114 (1926).

[3] W. H. Zachariasen, *Z. physik. Chem.*, **128**, 412 (1927); G. R. Levi and C. Fontana, *Gazz. chim. ital.*, **56**, 388 (1926), had previously reported some data without significant interpretation.

[4] M. L. Huggins, *Chem. Rev.*, **10**, 427 (1932); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[5] A. Ditte, *Compt. rend.*, **94**, 792, 864 (1882).

[6] R. L. Shriner and R. Adams. THIS JOURNAL, **46**, 1684 (1924).

0.006 Å. and $c_0 = 4.988 \pm 0.008$ Å., and that of stannous oxide to have $a_0 = 3.796 \pm 0.006$ Å. and $c_0 = 4.816 \pm 0.008$ Å. The Levi–Natta structure is eliminated by the fact that on the powder photographs of each substance the line {201} is observed while the line {111} is absent. Since the Lorentz, polarization, and temperature factors are all larger for {111} than for {201} and the frequency factor is the same, this observation shows that F^2_{201} is greater than F^2_{111}, whereas the Levi–Natta structure requires that F^2_{201} and F^2_{111} be equal.

This argument by which the Levi–Natta structure is eliminated is essentially the same as that used by Dickinson and Friauf, with Laue data, to eliminate this structure. We are unable to understand how Levi and Natta, with Dickinson and Friauf's paper available, could have been led to support the incorrect structure.

Our powder data for PbO and SnO are completely accounted for by the Dickinson–Friauf structure. The parameter z was evaluated as 0.2385 ± 0.0011 for PbO and 0.2356 ± 0.0019 for SnO. The method used was to find the values of z corresponding to the observed ratios of intensities of neighboring pairs of powder lines. In the calculations the James–Brindley f-values were used for oxygen, and Pauling–Sherman f-values for lead, tin, and palladium. In taking the averages the individual values were given equal weights. The indicated probable errors are three times the probable errors calculated from the internal consistency of the values.[7]

TABLE I

POWDER PHOTOGRAPHIC DATA FOR PbO AND SnO

Lines compared	Obsd. intensity ratio PbO	z
101:001	50.0	0.2410
110:001	21.0	.2408
200:102	25.0	.2389
112:102	42.0	.2388
220:212 + 113	13.3	.2405
114:104	8.0	.2380
002:102	17.7	.2388
103:212 + 113	21.3	.2391
213:104	18.0	.2370
312:104	13.0	.2350
204:214	6.5	.2380
	Average z = 0.2386	± 0.0011

Lines compared	Obsd. intensity ratio SnO	z
112:102	33.0	0.2380
220:212 + 113	3.0	.2350
114:104	5.0	.2355
213:104	11.2	.2329
312:104	8.8	.2337
204:214	5.8	.2387
Average z	= 0.2356	±0.0019

Our powder photographs of palladous oxide correspond to the tetragonal unit reported by Zachariasen, our values $a_0 = 3.02 \pm 0.01$ Å. and $c_0 = 5.31 \pm 0.01$ Å. being equal to within their probable errors to his. The photographs show only one reflection with $h + k + l$ odd, {100}.[8] The fact that no complex planes with $h + k + l$ odd are observed to reflect indicates very strongly that the heavy palladium atoms occupy body-centered positions, and the observed reflection {100} requires that the oxygen atoms then be not body-centered. There are three arrangements which satisfy these conditions:

2Pd at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
2O at (A) $\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, D^9_{4h}
(B) $\frac{1}{2}0\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$, D^9_{4h}
(C) $\frac{1}{2}0z$, $\frac{1}{2}0\frac{1}{2}+\bar{z}$, C^7_{4v}

The hemihedral arrangement C reduces to the holohedral arrangements A and B for $z = 0$ and $^1/_4$, respectively.

The oxygen atoms do not contribute to reflections with l odd. For l even the structure factor has the form

$$F = 2f_{\mathrm{Pd}} + 2f_{\mathrm{O}}(-1)^h(\cos 2\pi\, lz + i \sin 2\pi\, lz)$$

The following table gives the comparison of observed and calculated intensities for {112}, {101}, and {110}.

Reflection	Obsd. intensity	Calcd. intensity $z = 0$, A	$z = {}^1/_4$, B
{112}	27	15.7	26.4
{101}	90	90	90
{110}	18	17.8	17.8

It is seen that the agreement is unsatisfactory for $z = 0$ and satisfactory for $z = {}^1/_4$. In default of evidence for hemihedry, which would indicate some deviation of the parameter from the value $^1/_4$, we assume that the holohedral structure B is correct. All of our data are in satisfactory agreement with this structure, which is the structure suggested by Huggins.

No X-ray data have been reported previously for platinous oxide. Our preparation gave a

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(7) The results for stannous oxide are less precise than those for plumbous oxide because the preparation of stannous oxide used was very finely divided and gave diffuse lines, the intensities of which could not be estimated very accurately. Coarser preparations, consisting of very thin plates, gave anomalously high intensities for reflections {00l} because of orientation of the crystals.

(8) Neither Zachariasen nor Levi and Fontana reported the occurrence of this reflection. It appears clearly on our films.

powder photograph showing seven diffuse lines,[9] in positions corresponding to lines on the PdO photographs. The data are not sufficient to permit a rigorous structure determination to be made for PtO, but the similarity to the PdO photographs makes it highly probable that platinous oxide has the PdO structure; measurement of the three best lines ({101}, {103}-{200}, {211}) led to the unit dimensions $a_0 = 3.04 \pm 0.03$ Å., $c_0 = 5.34 \pm 0.05$ Å.

Discussion of the Structures.—In PbO and SnO each oxygen atom is surrounded tetrahedrally by four metal atoms (M–O–M bond angles 118° (4) and 105° (2)) and each metal atom is bonded to four oxygen atoms which form a square to one side of it (O–M–O bond angles 75° (4), 118° (2)). We suggest that the orbital arrangement for Pb^{II} and Sn^{II} in these crystals is that of a square pyramid, four bond orbitals being directed from the metal atom within the pyramid toward the four corners of the base and a fifth orbital, occupied by a stereochemically-active unshared electron pair, being directed toward the apex. The bond distance Pb–O is 2.30 ± 0.01 Å., and Sn–O is 2.21 ± 0.01 Å., corresponding to the radii 1.64 Å. for Pb^{II} and 1.55 Å. for Sn^{II}. These compare reasonably with known radii: Pb^{IV}, octahedral 1.50, tetrahedral 1.46; Sn^{IV}, octahedral 1.45, tetrahedral 1.40 Å. The Pb–Pb distances are 3.67 Å. (separate layers with oxygen layer between), 3.82 Å. (van der Waals contact), and 3.95 Å. (between atoms in the same layer); the corresponding Sn–Sn distances are 3.51, 3.70, and 3.80 Å.

In PdO and PtO each oxygen atom is surrounded tetrahedrally by metal atoms (M–O–M bond angles 98° (2) and 116° (4)), and each metal atom is at the center of a rectangle of oxygen atoms (O–M–O bond angles 82°, 98°). The distortion from the regular tetrahedron and square expected for oxygen and quadricovalent Pd^{II} and Pt^{II} represents a compromise required by the nature of the structure. The bond distances are Pd–O = 2.01 ± 0.01 Å. and Pt–O = 2.02 ± 0.02 Å., corresponding to square radii 1.35 Å. for Pd^{II} and 1.36 Å. for Pt^{II}.

Summary

Powder photographic X-ray data are used to show that the tetragonal crystal PbO has the structure assigned it by Dickinson and Friauf, and not that suggested by Levi and Natta. SnO has a similar structure.

$D_{4h}^7 - P4/nmm$: 2O at 000, $\frac{1}{2}\frac{1}{2}0$; 2Pb(Sn) at $\frac{1}{2}0z\ 0\frac{1}{2}\bar{z}$.
PbO: $a_0 = 3.947 \pm 0.006$, $c_0 = 4.988 \pm 0.008$ Å., $z = 0.2385 \pm 0.0011$.
SnO: $a_0 = 3.796 \pm 0.006$, $c_0 = 4.816 \pm 0.008$ Å., $z = 0.2356 \pm 0.0019$.

The tetragonal crystals PdO and PtO have a different structure (suggested by Huggins), in which the metal atom forms a coplanar rectangular coördination group.

$D_{4h}^9 - P4/mmc$: 2Pd(Pt) at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 2O at $\frac{1}{2}0\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$.
PdO: $a_0 = 3.02 \pm 0.01$, $c_0 = 5.31 \pm 0.01$ Å.
PtO: $a_0 = 3.04 \pm 0.03$, $c_0 = 5.34 \pm 0.05$ Å.

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[9] Some of the lines were much more diffuse than others; {110} and {112} gave very broad and apparently weak lines, much broader than the lines {101}, {103}-{200}, and {211}.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF CORNELL AND PRINCETON UNIVERSITIES]

The Structures of Methyl Borate and Trimethyl Triborine Trioxane. Interatomic Distances in Boron Compounds

BY S. H. BAUER AND J. Y. BEACH

The correlation of interatomic distances in compounds containing boron with the table of covalent radii[1] faces several difficulties. For many of the compounds investigated the use of the extrapolated radius (0.88 Å.) leads to the observed interatomic distances provided that resonance with several Lewis structures is considered; notable exceptions are the interatomic distances B–C, B–O, and B–F which would best be accounted for by assuming a radius in the neighborhood of 0.80 Å. Several proposals have been advanced to explain this divergence from additivity—in particular, Levy and Brockway[2] postulated that the short B–C distance in boron trimethyl is due to the incompleted valence shell (sp^2 type bonding) around the boron atom, and that the similar shortening in borine carbonyl is

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[1] L. Pauling and M. L. Huggins, *Z. Krist.*, **A87**, 205 (1934).

[2] H. A. Levy and L. O. Brockway, THIS JOURNAL, **59**, 2084 (1937).