

Studies on Mercury(II)oxide Chlorides and Mercury(II)oxide

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Several mercury(II)oxide chlorides have been described in literature, *viz.* $Hg_{n+1}O_nCl_n$ with $n = \frac{1}{2}, 1, 2, 3, 4, 5, 6,$ and 7^1 . In the course of studies of these substances the compounds with $n = \frac{1}{2}, 2, 3,$ and 4 have been synthesized and investigated by X-rays.

Hg_3OCl_4 . Colourless cubes. The cube edge $a = 9.24 \text{ \AA}$ and space group $P2_13$ are found in accordance with the data recently reported by Weiss *et al.*²

$Hg_5O_2Cl_3$. Black plates. Space group $P2_1/c$. Unit cell dimensions $a = 6.316 \text{ \AA}$, $b = 6.865 \text{ \AA}$, $c = 6.858 \text{ \AA}$, $\beta = 114^\circ 24'$ were in accordance with measurements by Gawrych³. The observed density 8.8 indicates a cell content of two formula units of $Hg_5O_2Cl_3$. The positions of the mercury atoms have been derived from projections of the Patterson function and corrected by "trial and error" methods giving

2 Hg in $2(a)$: 0, 0, 0

4 Hg in $4(e)$: $\pm(x, y, z), \pm(x, \frac{1}{2} + y, \frac{1}{2} - z)$
with $x = 0.425$, $y = 0.360$, $z = 0.265$.

It does not seem possible to arrive at a final decision on the arrangement of the chlorine and oxygen atoms from geometrical considerations. Attempts to attack the problem by means of Fourier methods are in progress.

$Hg_4O_3Cl_2$. Yellow needle-shaped crystals, apparently identical with the mineral kleinite (kindly supplied by Professor F. Wickman, Swedish Museum of Natural History, Stockholm).

$Hg_6O_4Cl_2$. Red crystals which form flat pyramids. Symmetry $P2_1/c$. Unit cell dimensions $a = 10.6 \text{ \AA}$, $b = 9.0 \text{ \AA}$, $c = 11.4 \text{ \AA}$, $\beta = 110^\circ$.

A determination of the crystal structure of mercury(II)oxide was carried out by Zachariassen⁴ on the basis of powder photographs. Weissenberg photographs of single crystals of montroydite and synthetic material, however, indicate a larger unit cell.

HgO . Space group $Pnma$. $a = 6.60 \text{ \AA}$, $b = 3.51 \text{ \AA}$, $c = 5.50 \text{ \AA}$. The positions of the mercury atoms are in fair agreement with those given by Zachariassen and it may

be that the superstructure is due to the arrangement of the oxygen atoms.

These investigations and also studies on mercury(II)oxide bromides are continued. Full reports will appear elsewhere.

1. Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Heidelberg 1914, p. 679—695.
2. Weiss, A., Nagorsen, G. and Weiss, A. *Z. anorg. Chem.* **274** (1953) 151.
3. Gawrych, E. *Gazz. chim. ital.* **56** (1926) 175.
4. Zachariassen, W. H. *Z. physik. Chem.* **128** (1927) 421.

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Acid-Induced Hydrogen Exchange in Benzene Derivatives as Electrophilic Aromatic Substitution

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Qualitative evidence, presented particularly by Ingold *et al.*¹, has shown that the hydrogen exchange induced by acids in benzene derivatives has the characteristics of an electrophilic aromatic substitution, *i. e.* a replacement of H^+ by H^+ . As quantitative measurements of the directing power of several substituents have been carried out for the common types of electrophilic aromatic substitution, especially nitration, it should be of interest to investigate the same influence on the hydrogen exchange.

Preparations of toluene, containing tracer amounts of toluene carrying tritium in its *ortho*, *meta*, *para*, and *alpha* positions, respectively, were shaken with 81.8 % sulphuric acid at $25^\circ C$ and the decay of the tritium content of the toluene was measured as a function of time. The experiments with the *alpha* substituted toluene showed that the methyl hydrogens do not exchange appreciably with the acid during the reaction times in question (maximum about two days). The results obtained with toluene-2-t, -3-t, and -4-t are shown in Figs. 1 and 2. From the initial slopes of the semilogarithmic curves the rates of tritium exchange were obtained², as the integrated rate expression cannot be used owing to the lack of