An X-Ray Investigation of the Hydrolysis Products of Mercury(II) In Solution

GEORG JOHANSSON

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

X-Ray scattering measurements have been made on concentrated hydrolyzed and non-hydrolyzed mercury(II) perchlorate solutions, prepared by dissolving HgO in HClO₄. In an acid solution, the Hg²⁺ ion coordinates about six water molecules at approximately equal distances (2.4 Å). Hydrolysis leads to a shortening of some of these Hg–O bonds and to the formation of polynuclear complexes in which the Hg–Hg distances are 3.64 Å. The average number of mercury atoms bonded to each mercury atom in the solution has been determined as a function of the degree of hydrolysis.

The ionic equilibria in hydrolyzed solutions of mercury(II) salts have been investigated by several workers, and the formation of polynuclear complexes has been suggested.¹ In an attempt to get direct information on the structures of these complexes, X-ray scattering measurements have now been made on hydrolyzed and non-hydrolyzed mercury(II) perchlorate solutions, prepared by dissolving HgO in perchloric acid. Series of solutions have been investigated, in which the total metal concentration and, as far as possible, the perchlorate concentration were kept constant, but the degree of hydrolysis, i.e. the amount of dissolved HgO, was varied.

EXPERIMENTAL

Preparation of solutions. The solutions were prepared by heating mercury(II) oxide (Merck p.a.) with perchloric acid (Merck p.a.) on a water bath, diluting to the required concentration, cooling to room temperature, and adding, to some of the solutions, sodium perchlorate to keep the ClO₄⁻ concentration constant. The composition of a solution was checked by analyzing for Hg²⁺ and ClO₄⁻. Mercury(II) was reduced by H₃PO₄ and precipitated and weighed as Hg₃Cl₄. The amount of perchlorate was determined by passing a portion of a solution through a cation exchanger and titrating the eluent with NaOH. The density was determined with a pycnometer. The compositions of the solutions are given in Table 1.

Three series of solutions with different total concentrations of Hg(II), 2 M, 3.5 M, and 4.6 M, were used. The largest solubility, about 0.25 mol of HgO per mol of Hg(II),

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Table 1. Composition of solutions in atoms per stoichiometric unit (= V Å³).

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>B1</th>
<th>B2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. of Hg²⁺</td>
<td>3.50 M</td>
<td>3.50 M</td>
<td>3.50 M</td>
<td>3.50 M</td>
<td>4.64 M</td>
<td>4.64 M</td>
</tr>
<tr>
<td>V Å³</td>
<td>474.37</td>
<td>474.37</td>
<td>474.37</td>
<td>474.37</td>
<td>365.87</td>
<td>357.82</td>
</tr>
</tbody>
</table>

Hg        | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
Cl        | 2.18 | 2.18 | 2.19 | 1.77 | 1.65 | 1.59 |
O         | 18.7 | 18.6 | 19.4 | 19.0 | 15.1 | 14.8 |
H         | 22.0 | 21.6 | 21.0 | 25.2 | 16.5 | 16.4 |
Na        | –    | 0.34 | 0.55 | 0.30 | –    | –    |

was obtained for the intermediate concentration. For the largest Hg(II) concentration, only hydrolyzed solutions could be prepared — in acid solutions mercury(II) perchlorate crystallized out. For the 2 M solutions, difficulties were encountered because of precipitation of insoluble compounds on the surface of the more hydrolyzed solutions during the X-ray measurements. The results obtained for those solutions that could be measured did not, however, differ from the more concentrated solutions, and will not be discussed further.

The solubility of HgO was limited by the formation of basic salts. Three different phases were found. In order of increasing basicity, they are: triclinic Hg₂O₃(OH)ₓ(ClO₄)ᵧ(H₂O)ₗ, orthorhombic Hg₂O₃(OH)ₓ(ClO₄)ᵧ, and monoclinic Hg₂O₃ClₓO₣. Their structures are closely related. They are all built up from infinite complexes and do not contain any discrete hydroxo complexes. The structure determinations will be published separately.¹,²

X-Ray scattering measurements. The X-ray scattering was measured from the free surface of the solutions, using MoKα radiation. The Bragg-Brentano focusing geometry was used. The diffractometer was essentially the same as described in previous papers,³ with the X-ray tube and the scintillation counter moving in opposite directions around the sample which was placed with the solution surface on the rotation axis of the diffractometer. A cylindrical radiation shield, provided with a beryllium window, enclosed the sample and hindered evaporation from the surface of the solution. Philips X-ray units PW1010 or PW1130 were used. Monochromatization of the scattered radiation was accomplished by means of a focusing single crystal LiF monochromator, placed on the counter side of the diffractometer. A further monochromatization was achieved by a pulse height discriminator. All measurements were made at 25°C.

The diffractometer is automatic, and measures and prints the time used for counting a preset number of counts (usually 40,000, corresponding to a statistical error of 0.5 %) at discrete values of θ (2θ = the scattering angle). The intervals in θ were 0.25°, except for the smaller angles (θ < 4°), where an interval of 0.1° was used. The range covered was 1° < θ < 70°. Opening slits of 1/12°, 1/4°, and 1° were used. Scaling factors for converting intensity values to the same slit width were obtained from measurements in overlapping regions. A check on the reproducibility of the intensity values was obtained by remeasuring each slit interval with larger steps in θ. These measurements were always the same within the statistical errors, and no corrections were required.

**TREATMENT OF THE DATA**

After converting the intensity data to a common slit width, it was corrected for polarization in the sample and in the monochromator. The amount of incoherent radiation slipping through the monochromator was estimated from the spectrum of the X-ray tube and the resolving power of the monochromator. For the outermost angles, it was experimentally determined by comparing the scattered intensity obtained with a Zr filter between the X-ray tube and the
sample with that obtained with the same filter between the sample and the monochromator. For $\theta = 65^\circ$, the amount of incoherent radiation was determined to be about 5% of the total scattered radiation.

The outermost range of the scattering curves ($\theta > 50^\circ$) was used for the scaling (Fig. 1). The independent coherent scattering, $\sum n_i f_i^2$, was calculated from the scattering factors ($f_i$), given by Cromer and Waber for the neutral atoms. The scattering factors were corrected for the real and the imaginary parts of the anomalous dispersion according to Cromer. The total amount of incoherent radiation was calculated from the values given in the International Tables for Cl, O, and Na. For H, Compton and Allison's values were used, and for Hg, estimates were made with the formula given by Bewilogua.

Reduced intensity functions $i(s) = I - \sum n_i f_i^2$ were obtained by taking the difference between the measured intensities after scaling, and the sum of the independent coherent scattering and the incoherent scattering. The radial distribution curves ($D(r)$) were calculated from the reduced intensity functions according to the expression

$$D(r) = 4\pi r^2 q_0 + 2r^2 \int_0^{s_{\text{max}}} s i(s) [f_{\text{Hg}}(0)/f_{\text{Hg}}(s)]^2 \exp(-ks^2) \sin(rs) \, ds$$

Here, $s = 4\pi \sin \theta / \lambda$, and $f_{\text{Hg}}(s)$ is the scattering factor of Hg for a value $s$. The average scattering density, $q_0$, is given by the square of the number of electrons per unit volume, which for all solutions was chosen to be the volume containing one Hg atom. The sharpening of the distribution curves obtained by the factor $(f_{\text{Hg}}(0)/f_{\text{Hg}}(s))^2$ was reduced by the exponential factor $\exp(-ks^2)$. Several different values for $k$ were tried, but the curves given here have all been calculated with $k = 0.012$, which seemed to be the best choice for minimizing false details in the curves without causing appreciable broadening of the peaks.

Pair interaction functions were calculated from

$$i(s) = \sum_{n,m} f_n f_m \sin r_{nm} s / r_{nm} s \exp(-bs^2)$$

Here, $r_{nm}$ is the distance between two atoms $n$ and $m$, $f_n$ and $f_m$ are the scattering factors, and $b$ is a temperature factor.

Least squares refinements were made by means of the LETAGROP program. A minimum was sought for the function $\Sigma(|s \cdot i_{\text{obs}}| - |s \cdot i_{\text{calc}}|)^2$.

The computer programs were written in such a way that the original intensity values and corresponding $s$ values were used throughout the calculations. No averaging in order to eliminate the statistical errors was made.

The following procedure for treating the data was used for all the solutions. After correction for polarization, scaling, and subtraction of incoherent radiation, the reduced intensities were calculated. Values with deviations from surrounding values which were clearly outside the limits, set by the statistical accuracy, were then excluded. Usually about 10 to 20 of the approximately 300 measured points were eliminated in this way. A new scaling was then made, and the radial distribution function was calculated. This usually showed small spurious peaks below 1 Å, which could not correspond to interatomic distances. They probably result from systematic errors corresponding to low-frequency additions to the reduced intensity functions, mainly due to small errors in the

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scattering factors or in the corrections made for incoherent radiation. The intensity values were corrected for these contributions by a Fourier inversion of the part of the radial distribution curve between 0 and \( \sim 1 \) Å. The expected contributions in this region from O–H distances at 1.0 Å and Cl–O distances at 1.45 Å were taken into account. The \( i(s) \) values given in Table 2 have been corrected in this way, but no such correction has been applied to the \( I \) values in that table. A survey of the measurements for one of the solutions is given in Fig. 1.

**ANALYSIS OF THE RADIAL DISTRIBUTION CURVES**

Distribution curves, \( D(r) \), are shown in Fig. 2, and \( D(r) - 4\pi r^2 q_0 \) functions in Fig. 3.

For all solutions, a peak occurs at 1.5 Å, which corresponds to the Cl–O distance of the perchlorate group. The acid solution shows only two more marked peaks, one at about 2.4 Å, which is the expected Hg–O distance for

Table 2. Observed intensities after scaling (I) and reduced intensities (i) as a function of s = 4π sinθ/λ for solutions A1, A4 and B2.

<table>
<thead>
<tr>
<th>s</th>
<th>I(s)</th>
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(X-ray investigation of Hg(II) solutions)

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at 3.6 Å, and a marked change occurs in the peak corresponding to the first coordination sphere of the Hg$^{2+}$ ion.

The 3.6 Å peak obviously represents Hg–Hg interactions in polynuclear hydrolysis complexes. It is close to the shortest of the Hg–Hg distances found in the basic mercury(II) perchlorates. The 2.4 Å peak is not well resolved in the $D(r)$ curves (Fig. 2). With increasing hydrolysis, it broadens and becomes less and less separated from the light atom interactions at about 3 Å.

The differences are more clearly brought out by using the distribution curve of the acid solution as an approximate reference line, and subtracting it from those of the hydrolyzed solutions. The resulting curves are given in Fig. 4. The effect of the second coordination sphere, which obscures the Hg–Hg peak in Fig. 3, is then largely eliminated, as it does not differ much for the different solutions. The resulting Hg–Hg peak seems to be symmetrical, and thus probably represents a single Hg–Hg distance in the complexes. The size of the peak corresponds to an average of about one Hg atom bonded to each Hg in the most hydrolyzed of the solutions. There are no clear indications of longer Hg–Hg distances.

The changes within the first coordination sphere of the Hg$^{2+}$ ion are clearly seen in the difference curves in the 1.5 to 2.5 Å region, to which only Hg–O interactions should contribute. Contributions from ClO$_4^-$ groups at 1.5 Å (Cl–O) and 2.4 Å (O–O) are the same as in the acid solution, and cancel out. For those solutions in which the ClO$_4^-$ concentrations are slightly lower (Table 1), the differences have been compensated by adding calculated contributions from Cl–O and O–O interactions. Light atom interactions, primarily O–O contact distances, are small in this region, and should not differ significantly for the different solutions. Thus the positive peaks at 1.95 Å and the negative peaks at 2.35 Å in Fig. 4 can be uniquely ascribed to changes in Hg–O interactions. The occurrence of these peaks shows that in the hydrolyzed solutions, Hg–O distances must occur, which are shorter than about 2.1 Å, and which are not present in the acid solution. The negative peak at 2.35 Å indicates that in comparison with the acid solution, fewer and slightly longer distances occur in this region.

An analysis of the Hg–O peak in the distribution curve for the acid solution, made by comparison with calculated Hg–O peak shapes, assuming different temperature factors for the Hg–O interaction, shows no indication of the presence of diaquo ions. This is illustrated in Fig. 5, which compares the experimental $D(r)$ curve for the acid solution with calculated Hg–O peaks in the 1.5 to 2.5 Å region. The experimental curve has the same shape as that calculated for six oxygen atoms at equal distances (2.34 Å). It differs clearly from the shape calculated for two oxygens at 2.0 Å and 4 oxygens at 2.5 Å, which are the approximate distances expected for a diaquo ion. Similar results

*Fig. 4.* Difference functions obtained by subtracting the curve for the acid solution in Fig. 3 from the corresponding curves for the hydrolyzed solutions. The calculated curve at the top of the drawing was obtained by subtracting the peak shape for six Hg–O interactions at 2.34 Å from that for two Hg–O at 2.0 Å, and four Hg–O at 2.5 Å and multiplying the result with 0.7, to correct for the presence of unhydrolyzed Hg$^{2+}$. The dots indicate peak shapes for Hg–Hg interactions, calculated with the use of the parameters from the least squares refinement.
have previously been reported by van Eck, who measured the X-ray scattering from 2 M solutions of Hg(BF$_4$)$_2$. He concluded that in these solutions, the Hg$^{2+}$ ion was octahedrally coordinated by six water molecules at 2.33 Å.

The change in the coordination around the mercury ion caused by the hydrolysis and illustrated by the difference curves in Fig. 4 can now be explained as the result of a shortening of some of the Hg – O bonds. The observed difference curves can be closely reproduced by assuming that in the hydrolysis products, about two Hg – O bonds are shortened to 2.0 – 2.1 Å, and the remaining four bonds lengthened to about 2.5 Å (Fig. 4), compared with the approximately equal distances of 2.3 Å around the unhydrolyzed Hg$^{2+}$ ion. Although the estimate of the number of bonds affected by these changes is at best approximate, the estimates of the resulting distances are more exact, since even small changes in the assumed distances cause drastic changes in the calculated difference curves, which are clearly inconsistent with those observed.

**ANALYSIS OF THE REDUCED INTENSITY FUNCTIONS**

For a closer analysis of the Hg – Hg interactions, the intensity curves are more suitable than the distribution curves, in which the presence of the broad background peak from the second coordination sphere interferes with the Hg – Hg peak. The broad peak corresponds to highly damped contributions to the intensity function, while the sharp Hg – Hg peak results from contributions over a much larger range of $s$ values. This makes a separation of the two contributions possible by a direct analysis of the $i(s)$ values, for example by means of a least squares procedure. Such an analysis also has the advantages that the direct connection to the measured data allows an estimate of the statistical errors in the parameters, and each intensity value can be given a weight corresponding to its statistical accuracy.

Theoretical intensity values were calculated as a sum of pair interaction functions. A Hg – O distance at 2.4 Å, a Hg – Hg distance at 3.6 Å, and another Hg – O distance at 4.2 Å, approximating the many different Hg – O interactions in that region, were included. To this was added contributions from the perchlorate ions, assuming the ClO$_4$ group to be a regular tetrahedron with a Cl – O distance of 1.45 Å. For each pair interaction, three parameters
Fig. 6. Reduced intensity functions, $i(s)$, after multiplication by $s$, referred to a stoichiometric unit of solution, containing one mercury atom. About one third of the number of observed values, chosen at random, are indicated. The full-drawn curves represent $i(s)$ values calculated with the parameters from the least squares refinement.

Fig. 7. Calculated $s$ $i(s)$ values and peak shapes for the interactions included in the least squares refinement of the scattering data from solution A4. The calculations are based on the parameters in Table 3.

were introduced: the distance, the number of interactions, and a temperature factor. These were refined, as was also a scaling factor, by a least squares procedure, to get the best agreement between observed and calculated intensities.

The refinement was carried out in several steps. Firstly, the intensity values for $2.7 < s < 16$ were used, to refine the short Hg–O and the Hg–Hg interactions with no other Hg–O distances included. The region $1 < s < 16$
was then used to refine simultaneously the Hg–Hg distance and the longer Hg–O distance (4.2 Å), keeping other parameters constant. This refinement converged, indicating that the two interactions could be resolved. Finally, the region $2.5 < s < 14$ was used to refine the Hg–Hg and the short Hg–O distances without varying the parameters of the longer Hg–O distance, the contributions of which are very small in this region of the intensity curves. The refinements were continued until the shifts were well below the calculated standard deviations.

The parameters of the Hg–Hg interaction, which are the ones of interest, did not vary significantly between the different refinement steps. The final parameters and the standard deviations are given in Table 3. The agreement between observed and calculated intensities is shown in Fig. 6. The average number of Hg neighbours at 3.64 Å from each Hg atom is given in Fig. 8 as a function of the degree of hydrolysis. For the most hydrolyzed of the solutions (A4), the contributions of the various interactions to the intensity curves and their corresponding peak shapes are compared in Fig. 7.

Table 3. Result of the least squares refinement of the $i(s)$ curves. $d =$ distance in Å, $n =$ number of distances per Hg atom, $b =$ temperature factor. Standard deviations are given within brackets.

<table>
<thead>
<tr>
<th>Soln. No.</th>
<th>Hg–Hg</th>
<th>(Hg–O)$_1$</th>
<th>(Hg–O)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d$</td>
<td>$n$</td>
<td>$b$</td>
</tr>
<tr>
<td>A1</td>
<td>2.42(1)</td>
<td>5.7(3)</td>
<td>0.019(2)</td>
</tr>
<tr>
<td>A2</td>
<td>2.41(1)</td>
<td>5.4(4)</td>
<td>0.030(5)</td>
</tr>
<tr>
<td>A3</td>
<td>2.43(2)</td>
<td>6.5(5)</td>
<td>0.047(7)</td>
</tr>
<tr>
<td>A4</td>
<td>2.44(1)</td>
<td>6.8(2)</td>
<td>0.052(2)</td>
</tr>
<tr>
<td>B1</td>
<td>2.43(1)</td>
<td>6.0(5)</td>
<td>0.043(6)</td>
</tr>
<tr>
<td>B2</td>
<td>2.41(1)</td>
<td>4.9(4)</td>
<td>0.036(3)</td>
</tr>
</tbody>
</table>

Fig. 8. Number of Hg neighbors at 3.64 Å around each Hg atom as a function of $H$, the analytical hydrogen ion excess (referred to a 3.5 M solution). Observed values are indicated by crosses (3.5 M solutions) or dots (4.6 M solutions). The standard deviation, calculated in the least squares refinement, is given for each point.

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DISCUSSION OF THE RESULTS

The hydrolysis of the mercury(II) solutions has a rather small effect on the scattering curves, because only low-nuclear complexes seem to be formed, and because concentrations of the hydrolysis complexes are small. Even in the most hydrolyzed of the solutions, about one third of the mercury should still be unhydrolyzed, according to the stability constants given by Ahlberg. In the \( D(r) \) curves (Fig. 2), no well-resolved peaks are present, which can be used to follow the changes.

However, by working in solutions with, as nearly as possible, the same compositions, the small differences, caused by the hydrolysis, can be analyzed, since contributions to the scattering from distances other than those involving Hg atoms should be fairly constant for the different solutions. The difference curves in Fig. 4, should then give the best representation of the changes. This should be true at least for the 2 to 2.5 Å region, where Hg—O interactions are the main contributors. The splitting up of the Hg—O distances in the hydrolysis complexes, compared with the more equal distances around the unhydrolyzed \( \text{Hg}^{2+} \) ion, is shown clearly by the distribution functions and especially by the difference curves. In the least squares refinement, this change in coordination is seen mainly as an increased temperature factor for the single Hg—O interaction introduced (Table 3).

In the region 3.5 to 4 Å, where the Hg—Hg distance in the hydrolysis complexes appears, a great many other distances also contribute, and it seems likely that those related to a second coordination sphere around the Hg atom could to some extent change with hydrolysis. In a polynuclear complex, well-defined longer Hg—O distances must occur within the complex, which are not present around an unhydrolyzed \( \text{Hg}^{2+} \) ion, and these differences may affect the Hg—Hg peaks in the difference curves. A least squares refinement of the parameters of the Hg—Hg interaction, using the observed intensity values, should be less sensitive towards such changes, because the spread of distances within the second coordination sphere should lead to highly damped contributions to the intensity function, and also because such changes at least to some extent can be taken up by the parameters introduced. On the other hand, these second-coordination sphere interactions have been approximated by a single Hg—O interaction with a large temperature factor, which may not correspond to the actual distribution of distances.

Other distances than those now used for the refinement can be introduced in the least squares procedure by using reasonable assumptions for their distributions. It seems preferable, however, to exclude such contributions when refining the intensity values, and to minimize the errors made by not using the first part of the intensity curves, where these interactions have their main contributions. The good agreement between observed and calculated intensities down to values of \( \theta = 1 \), as shown in Fig. 5, supports the assumption that no great errors are made by the exclusion of other distances in the solutions. As a further check on the number of Hg—Hg interactions obtained in the refinements (Table 3), corresponding peak shapes were calculated and were compared with the difference curves (Fig. 4). Although the least squares refinements and the difference curves should be differently affected by systematic errors,
the agreement is good. The error estimates made in the least squares process thus seem to be reliable.

CONCLUSIONS

According to the X-ray measurements, two main changes occur when a solution of mercury(II) perchlorate is hydrolyzed. The coordination of the mercury ion is changed, leading to a shortening of some of the Hg—O distances within the first coordination sphere. Polynuclear complexes are formed, in which the Hg—Hg distances are 3.64 Å. In the most hydrolyzed of the solutions investigated, corresponding to a removal of about 0.5 hydrogen ions per hydrated mercury(II) ion, each mercury atom is bonded to an average number of about one other mercury atom. Taking into account that about one third of the mercury in this solution, as calculated from the stability constants given by Ahlberg, is still unhydrolyzed, the average number of Hg atoms bonded by each Hg atom in the hydrolysis complexes is larger than one. Thus the condensation does not stop at dinuclear complexes. However, since longer Hg—Hg distances are not clearly indicated in the radial distribution curves, the dominating complexes in the solutions must still be of a low nuclearity.

An interpretation of the results in terms of possible structures of the hydrolysis complexes can be made by combining information obtained from the X-ray scattering measurements with that from equilibrium measurements and crystal structure determinations, and will be given in a following paper.

Acknowledgements. My thanks are due to Ernst Hansen and Anita Johansson for assistance in the work, and to Dr. Peter Staples for corrections of the English of the manuscript.

The work has been supported by Statens Naturvetenskapliga Forskningsråd (Swedish Natural Science Research Council). Computer time has been made available by the Computer Division of the National Swedish Office for Administrative Rationalisation and Economy.

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Received December 28, 1970.

Acta Chem. Scand. 25 (1971) No. 8