[CONTRIBUTION NO. 523 FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Interatomic Distances in Orpiment, Realgar, Sodium Sulfantimonate Enneahydrate, and Calcium Mercuric Bromide[1]

BY WILLIAM V. MEDLIN

The method of direct determination of radial distribution of atoms from x-ray photographs was first used by Debye and Menke,[2] who applied it to mercury as an example of a monatomic liquid substance. It was extended by Gingrich and Warren[3] to solid substances, both crystalline and amorphous. In this field it has been found to be quite useful in determining distances between heavy atoms as a preliminary step in the determination of crystal structures, and in studying the bonding between atoms without determining complete structures. With the latter purpose in view I have applied the method to orpiment, realgar, sodium sulfantimonate enneahydrate, and calcium mercuric bromide. In all cases an approximate form of the method was used, in which visual estimates of the intensities of the lines of the powder photograph replaced the absolute intensities required by the formula, thus making impossible a quantitative measurement of the scattering power of the atoms concerned. The distances obtained by the rough treatment, however, are quite reliable, as shown by the fact that reasonable changes in the estimates of the intensities do not alter appreciably the positions of the peaks in the resulting distribution curves.

The method of treatment was the same as that used with diphenyliodonium iodide in a previous work.[4] The samples were all mounted with collodion on the outside of fine tubes of low absorbing glass; the radiation used was the Kα line of copper, obtained by passing copper radiation through nickel. The estimated intensities of the lines on the resulting photographs were multiplied by a small arbitrary factor, $e^{-B\sin^2\theta}$ and used directly as I_i in the formula

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\sum_{i=1}^{\infty} s_i I_i \sin s_i r$$

where $s = (4\pi \sin \theta)/\lambda$ and θ is one-half the angle of scattering. ρ_0 is a constant proportional to the number of scattering electrons per unit volume; its value is not known if absolute values of the intensities are unknown. The curves shown in this article do not include this term.

Orpiment and Realgar

Orpiment and realgar are naturally occurring sulfides of arsenic; the stoichiometrical formula of the former is As_2S_3 and that of the latter AsS. Both are monoclinic; measurement of the layer lines on a rotation photograph of orpiment gave $b = 11.41 \pm 0.05$ Å. The axial ratios of orpiment are $a:b:c = 0.5962:1:0.6650$ with $\beta = 90°41'$.[5] In orpiment the coördination numbers of arsenic and sulfur can be three and two, respectively, with each arsenic atom bonded to three sulfur atoms and each sulfur bonded to two arsenic atoms. If the same coördination numbers are to prevail in realgar there must be As–As bonds, with each arsenic atom bonded to another arsenic and two sulfur atoms. The normal As–As distance is 2.42 Å., and the As–S distance should be 2.25 Å., from the corresponding covalent radii.[6] We may expect that application of the radial distribution method will disclose those bonds that exist.

Powder photographs of the two substances are quite different in arrangement of their lines; their similarity lies in the fact that the strongest lines of both patterns occur at approximately the same scattering angles. We see from Fig. 1, calculated with the use of 45 and 74 powder lines, respectively, that the resulting radial distribution curves are alike in the interesting region with r less than 5.5 Å. In the case of orpiment the first small peak occurs at $r = 2.24$ Å., the second peak at 3.46 Å., and a third at 4.39 Å. In the curve for realgar the first peak is at 2.16 Å., the second at 3.54 Å., and the third at 4.52 Å. Only the first peak in each case may be attributed to two atoms that are bonded together; the position of the peaks is correct for the As–S separation. In realgar a peak representing the As–As bond should be one-half as important as the As–S peak, since there must be four As–S bonds for each As–As bond, and the atomic number of arsenic is approximately twice that of sulfur. Hence if there

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(1) Original manuscript received February 20, 1936.

(2) Debye and Menke, *Physik. Z.*, **31**, 419 (1930).

(3) Gingrich and Warren, *Phys. Rev.*, **46**, 368 (1934).

(4) Medlin, THIS JOURNAL, **57**, 1026 (1935).

(5) Groth, "Chemische Kristallographie," Engelmann, Leipzig.

(6) Pauling and Huggins, *Z. Krist.*, [A] **87**, 205 (1934).

are As–As bonds at 2.4 Å. we might observe that a separate peak exists to represent it or that a single peak occurs at a value of r somewhere between the As–S and As–As separations, and closer to the former. Actually the observed peak is at a slightly smaller value of r than expected.[7]

If in orpiment we assume coördination numbers of three and two, respectively, for arsenic and sulfur we must attribute the first peak to the As–S bond and the second peak to unbonded As–As interaction with the x-ray beam. On this basis we can calculate for the bond angle for sulfur the value 97°14′. The third peak represents a distance more than twice that between sulfur and arsenic, and thus it cannot represent the nearest S–S distance. This distance must then be approximately 3.4 Å. and the arsenic bond angle approximately that of sulfur. The comparatively low scattering power of sulfur makes measurement of the S–S distance much less reliable and increases the reliability of the As–As distance obtained. A similar calculation for realgar gives the value 102°32′ for a bond angle, perhaps the average for sulfur and arsenic.

Sodium Sulfantimonate Enneahydrate (Schlippe's Salt)

Sodium sulfantimonate enneahydrate, $Na_3SbS_4 \cdot 9H_2O$, was treated by this method, using 86 powder lines, with the result shown in Fig. 1. The first peak occurs at 2.26 Å., and must be attributed to the Sb–S interaction as being by far the most important at this small distance. The second peak is found at $r = 4.31$ Å.; this is presumably an average S–S distance, with perhaps other distances involving atoms of smaller atomic numbers also contributing, unresolved from the main peak. It is interesting to note the simplicity of the radial distribution curve for a substance consisting of many light atoms; we see that resolution of distances involving these atoms is quite poor. In order to resolve distances in such cases it would be necessary to use accurate intensities to much larger values of $(\sin \Theta)/\lambda$.

The Sb–S distance found for this substance is appreciably smaller than the sum of the normal covalent radii for sulfur and antimony, 2.40 Å. It was suggested in a similar observation by Brockway and Wall[8] on stannic chloride and similar compounds that differences in residual charge on the atoms act in shortening the bonds between them, and that double bonded structures may be contributing to some extent to the normal state of the molecule. Both suggestions are valid in this case.

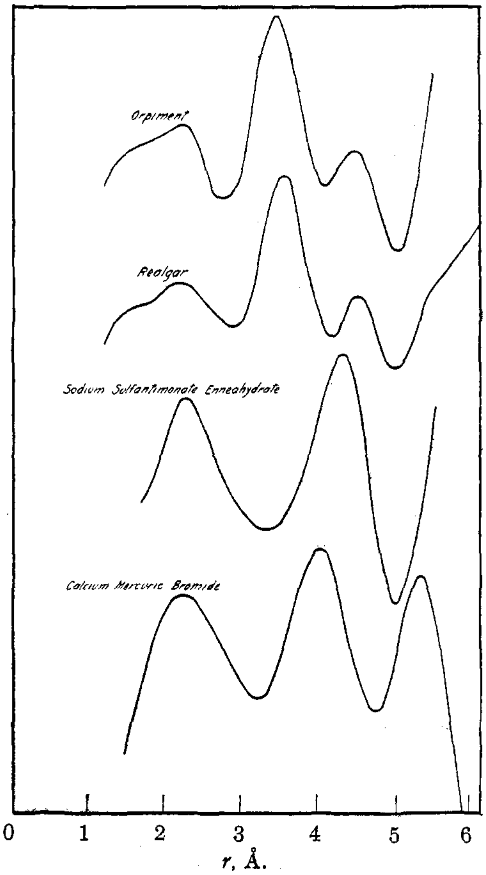

Fig. 1.

Calcium Mercuric Bromide[9]

Figure 1 also shows the density distribution curve obtained for calcium mercuric bromide, $CaHgBr_4$, with the use of 61 powder lines. The three peaks shown occur at 2.24 Å., 4.01 Å. and 5.35 Å. The first peak is rather broad, indicating that several rather widely differing unresolved distances are contributing. It is likely, then, that the value 2.24 Å. does not represent accurately a single Hg–Br distance, but that there are several such distances existing in the crystal. If there are $HgBr_4$ tetrahedra and the position of the second peak is taken to represent the Br–Br distance, the Hg–Br distance is calculated to be 2.47

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(7) M. J. Buerger, *Am. Mineral.*, **20**, 36 (1935) reports $a_0 = 9.27$ Å., $b_0 = 13.50$ Å., $c_0 = 6.56$ Å., $\beta = 73° 22.7'$, 16 AsS, space group $C_{2h} - P_2/n$ for realgar.

(8) Brockway and Wall, THIS JOURNAL, **56**, 2373 (1934).

(9) It was shown in 1922 by Professors R. G. Dickinson and L. Pauling that the face-centered cubic unit of structure of this crystal has $a_0 = 19.14$ Å. and contains 32 $CaHgBr_4$ (unpublished investigation).

Å. If on the other hand the structure is built upon bromide ions in contact, the Br^-–Br^- distance would be expected to be approximately 3.90 Å., the diameter of the bromide ion,[10] agreeing with the observed position of the second peak.

Conclusion

Application of the rough radial distribution method of these four substances shows in a general way to what extent the method may be relied upon. The results seem to be accurate when there is only one distance involving large atoms near a given value; otherwise resolution is poor. In a large number of cases in which the structure is not known it is impossible to state whether or not this condition is being fulfilled. The use of reflections at large values of $(\sin \Theta)/\lambda$ gives increased resolutions; with intense photographs and accurate estimates of intensities of the weak lines being reflected at large angles one could use these important lines to much greater advantage. It is a particularly useful method when applied to large molecules containing a comparatively small number of heavy atoms.

I wish to express my gratitude to Professor Linus Pauling for his valuable coöperation, and to Dr. Sidney Weinbaum for his assistance in preparing the curves for presentation.

Summary

The radial distribution method has been applied to orpiment, realgar, sodium sulfantimonate enneahydrate and calcium mercuric bromide. The environment about the atoms in realgar is shown to be remarkably like that in orpiment, and in both cases the distance between arsenic and sulfur atoms agrees within experimental error with the sum of the corresponding covalent radii. A value for the sulfur bond angle is given, and the *b*-axis of the unit cell of orpiment was measured. The sulfur–antimony distance in sodium sulfantimonate enneahydrate was found to be definitely less than the sum of the covalent radii. Application of the method to calcium mercuric bromide led to indefinite results, consistent either with a closest packing of bromide ions, or with a structure consisting of tetrahedral covalent $HgBr_4$ groups.

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[10] Pauling, THIS JOURNAL, **49**, 765 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, TEMPLE MEDICAL SCHOOL]

Improvements in Technique for the Determination of Microgram Quantities of Iodine

BY R. H. HAMILTON, JR.[1]

Because a small amount of iodine has to be extracted from a large mass of other salts before determination, and because extraction with alcohol, as advocated by von Fellenberg,[2] requires the iodine to be in the form of iodide, it is necessary to reduce iodates that may be present. Such reduction has been done in the past with sulfites in acid solution. Acidification increases the amount of salts present, and thus increases the difficulty of extraction, because the salt mixture must again be made alkaline before extraction with alcohol.

Harvey[3] used hydrazine sulfate to reduce iodate when purifying potassium hydroxide solutions. He did not show how nearly quantitative such reduction was. In the present investigation hydrazine sulfate was found to give quantitative reduction. Hydrazine hydrate was later tried and found to have the same action. It should be preferable to the sulfate, as the excess is completely volatile when hydrate is used, whereas added sulfate ions remain as potassium sulfate. When an excess of hydrazine sulfate or hydrate has been added, a small drop of carbonate solution produces a dark spot when placed upon paper dipped in a 5% mercuric chloride solution and dried.

The salt mixture from which iodide is to be extracted usually contains much potassium carbonate, since von Fellenberg advocated the use of this substance.[2] The usual practice has been to evaporate the solution until a solid phase of carbonate appeared. Then the two-phase system was extracted by rubbing with alcohol, which formed a third phase. Occlusion of iodide by crystals becomes marked if there is no aqueous phase present. This fact suggested the use of a two-phase system consisting of saturated potas-

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[1] National Research Fellow in the Biological Sciences, 1934–1935.

[2] Th. von Fellenberg, *Biochem. Z.*, **139**, 391 (1923).

[3] C. O. Harvey, *Analyst*, **59**, 479 (1934).