

Hydrolysis of Osmium Compounds

THE chemical determination of the atomic weight of osmium made by Gilchrist¹ in 1932 gave the value of 191.5. This result was accepted internationally until Nier² calculated the value 190.2, now accepted as the international value, from mass spectrographic data. The method used by Gilchrist involved the ignition of ammonium hexabrom- and hexachlorosmate IV in hydrogen to osmium metal. The ammonium hexahalogenates were crystallized several times from 7 or 10 per cent halogen acid.

The possibility of hydrolysis during crystallization to the hydroxy pentahalogenates which would lead to high values for the atomic weight was discounted by Gilchrist on the basis that both the compounds at either acid concentration gave concordant results. It might be pointed out that the difference in the two acid concentrations is not great enough to affect noticeably the extent of hydrolysis; and further, since the chloro compound can be expected to hydrolyse more than the bromo compound, the differences in the osmium content consequent on partial hydrolysis would be nearly identical.

Mellor³ noted subtle differences in the colours of specimens of ammonium hexabromosmate used for magnetic measurements and suggested that the high atomic weight by the chemical method might be due to hydrolysis.

While investigating the colorimetric micro-determination of osmium, we noted that the osmium content of ammonium bromosmate seemed to vary with the previous history of the specimen. To confirm the observation, pure ammonium hexabromosmate was prepared by dissolving pure osmium tetroxide in 50 per cent hydrobromic acid at room temperature, precipitating with cold saturated ammonium bromide solution, and washing with ice water and absolute alcohol. The substance was dried in vacuum over concentrated sulphuric acid. Portions were afterwards crystallized once from various concentrations of hydrobromic acid, and dried as before. The osmium content was found by ignition in ammonia gas at 450°.

Material	% Osmium
Pure (theoretical) (NH ₄) ₂ OsBr ₆	{ 26.95 (calc. from at. wt. of Os = 190.2) 27.08 (calc. from at. wt. of Os = 191.5)
Crystallized from 50% HBr	26.97; 27.01
Crystallized from 10% HBr	27.12; 27.11
Crystallized from 1% HBr	28.37; 28.28

It is of interest to note that specimens crystallized once from 1 per cent hydrobromic acid, then several times from 50 per cent acid, did not change in osmium content, suggesting that, as with the corresponding ruthenium compound, the hydrolysis is not easily reversed. From the analyses for bromine and osmium the substance is hydrolysed approximately 50 per cent by crystallization from 1 per cent hydrobromic acid. The crystal structures of these partially hydrolysed materials, which appear to be homogeneous, are at present being examined.

F. P. DWYER
N. A. GIBSON

Department of Chemistry,
University of Sydney,
Sydney.
Feb. 1.

¹ Gilchrist, *J. of Res., U.S. Bur. Stand.*, **2**, 279 (1932).

² Nier, *Phys. Rev.*, (ii), **52**, 885 (1937).

³ Mellor, *J. Roy. Soc. N.S.W.*, **77**, 145 (1943).

Constitution of Ferri-Phenol Complex in Solution

OUR knowledge as to the constitution of the coloured compound formed by the interaction of phenol with freshly prepared ferric chloride solution is very meagre. Brode and Wesp¹ suggested that the violet-red colour is probably due to an ion of the type $[\text{Fe}(\text{OPh})_6]^{-3}$; but they have not presented any evidence in its favour. We have studied the reaction by four different methods: thermometric, conductometric, absorption and transport measurements. Thermometric and conductometric titration curves of phenol with ferric chloride solutions show two breaks corresponding to Fe^{+3} : phenol equal to 1:3 and 1:6; so these may be supposed to represent the formation of the compounds $\text{Fe}(\text{OPh})_3$ and $\text{H}_3[\text{Fe}(\text{OPh})_6]$. By applying Job's method of continued variation, it is found that, for equimolecular solutions, the maxima in the optical density curve against the volume of one of the reactants appear at the point Fe^{+3} : phenol equal to 1:3. The maxima of the curves are found to be independent of the wave-length (490 μ , 550 μ) and the concentration of the reactants used, and so are due to the formation of the compound $\text{Fe}(\text{OPh})_3$. Now the compound $\text{Fe}(\text{OPh})_3$ may also be formulated as $\text{Fe}[\text{Fe}(\text{OPh})_6]$, in which case also the ratio of Fe^{+3} : phenol is equal to 1:3. When ferric chloride-phenol solutions are shaken with non-polar organic solvents, the coloured compound is not found to be partitioned between the two liquid phases, and this supports the formulation of $\text{Fe}(\text{OPh})_3$ as $\text{Fe}[\text{Fe}(\text{OPh})_6]$. Finally, transport experiments by Duval's apparatus with solutions containing ferric chloride and phenol in the ratio 1:3 show that iron goes to the anode and thus give additional and direct evidence in favour of the formulation $\text{Fe}[\text{Fe}(\text{OPh})_6]$.

Further studies with other phenols and phenolic acids are in progress and the results will be published soon.

Our thanks are due to Prof. P. B. Sarkar for his interest and for laboratory facilities.

SUKUMAR BANERJEE

BARUN CHANDRA HALDAR

Ghose Professor's Laboratory of Chemistry,
and Inorganic Chemistry Laboratory,
University College of Science and Technology,
92 Upper Circular Road, Calcutta 9, India.

¹ Brode, W. R., and Wesp, E. F., *J. Amer. Chem. Soc.*, **56**, 1037 (1934).

An Auroral Spectrogram Obtained at Oslo on February 23

UP to the present at Tromsø and Oslo we have observed and measured about 170 vibrational bands and atomic lines in the auroral luminescence; but only the somewhat stronger ones have been obtained with spectrographs having a dispersion sufficiently great to give the wave-length with the accuracy wanted for a reliable identification of the lines.

On spectrograms of fairly small dispersion a number of lines have been seen to exist, which are not well separated, but form more or less continuous bands. For spectral analyses, particularly of the weak lines and bands, I have got a large new spectrograph, which was built in accordance with my specifications by the Société Générale d'Optique of Paris. This spectrograph, which is very accurately made, combines a high light-power with a dispersion so great that the wave-length of a sharp line