ON THE ACTION OF 66° SULPHURIC ACID ON HYDROCHINON AND THE VALUE OF THE RESULTING SULPHO ACID AS A DEVELOPER FOR GELATINO-BROMIDE PLATES.

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PRELIMINARY NOTICE.

Since the introduction of the dry plate in photography many substances have been proposed as developers, but the only practical survivors of the substances thus proposed are pyrogallic acid, ferrous oxalate, hydrochinon, and more recently eikonogen, or the sodium salt of amido-β-naphtholmonosulpho acid. Having at one time had occasion to employ hydrochinon as a developer, I was struck with the beautiful qualities of the plates developed by its means, but, although hydrochinon is *per se* a most excellent developer, it has, nevertheless, several drawbacks, among which are its limited solubility in water, and it was this very question of solubility which started me upon the present investigation. It seemed that if hydrochinon could be converted into a mono-sulpho acid, that its solubility would be very materially increased, and if this could be accomplished without in any way affecting its reducing qualities for the haloid salts of silver, a very material improvement would be obtained.

Finding only very meagre information in the literature upon this subject the following experiments were made.

EXPERIMENT 1.

20 grams of 66° sulphuric acid were mixed with 10 grams of hydrochinon, and then heated under constant stirring upon the steam bath, until the hydrochinon was all dissolved. The stirring was kept up for a few minutes longer, when suddenly the whole contents of the beaker solidified to a cake of small straw colored needles.

The cake was broken up and dissolved in cold water, in which it is very soluble, then converted into its lime salt by neutralizing the acid solution with calcium carbonate. The precipitate of calcium sulphate was filtered off and the filtrate of the lime salt placed upon the steam bath for concentration. After a short exposure to the air the solution began to darken, showing that oxidation was taking place. Concentration by this means had therefore to be abandoned. The solution was then placed under the air pump over sulphuric acid, hoping that by this means it may be concentrated without spoiling, but even in this case oxidation kept slowly taking place. It was therefore decided to treat the mixture with an excess of sodium sulphite and then concentrate in vacuo over sulphuric acid. On adding the sodium sulphite calcium sulphate was precipitated carrying considerable of the coloring matter with it. The precipitate was filtered off, and the filtrate containing the sulpho acid of hydrochinon was placed under the bell jar of the air pump over sulphuric acid, to concentrate, but owing to an accident, the contents of the beaker were spilled, and therefore the experiment had to be repeated.

EXPERIMENT 2.

10 grams of hydrochinon were treated as before with 20 grams 66° sulphuric acid. After the reaction the mixture was dissolved in water, heated upon the water bath, and neutralized with barium carbonate.

The barium sulphate was filtered off, and the filtrate containing the barium salt of the sulpho-acid was concentrated in vacuo over sulphuric acid. The barium salt thus obtained crystallized much more readily than the calcium salt and the solution of the same in water does not appear to be as readily oxidizable as the former when exposed to the air. It crystallizes from its aqueous solution in white, warty concretions of star-grouped crystals (needles).

A sample of the above barium salt obtained by rapidly boiling down a portion of its aqueous solution to dryness and then further drying over sulphuric acid gave the following results :

Water of Crystallization.

0.2810 grm. substance lost 0.0081 grm. H_2O
equivalent to water 2.88 per cent., or 1 mol. water of crystallization.

Ba. Estimation.

0.2810 grm. sub. gave 0.116 grm. Ba SO$_4$

Equivalent to Ba......................24.26 per cent.
Equivalent to Ba. in anhydrous salt......24.98   "

On now attempting to calculate the molecular weight ·of the barium salt from the amount of barium sulphate formed, we get the following :

0.2729 anhydrous salt gave 0.116 gram. Ba.SO$_4$.

.116: 233 (BaSO$_4$) :: 0.2729 : x ; x = 548.1

The least molecular weight of the salt, carrying one atom of barium, is therefore 548.1.

One atom of barium might belong, however, to a substance containing either one or two sulpho-groups ; but, the theoretical molecular weight of barium hydrochinon disulphonate is 406, whereas the theory for barium hydrochinon monosulphonate is 515, (calculated from the formulæ $\left(\text{p.} \, C_6 \, H_3 \left< \begin{array}{c} \diagup OH \\ \underline{}SO_3 \\ \diagdown OH \end{array} \right)_2 Ba, \right)$ and consequently the former is excluded. Therefore the substance analysed is beyond much doubt the barium salt of a hydrochinon mono-sulpho acid.

On calculating the molecular weight from the salt containing water of crystallization we get :

0.116 : 233 :: 0.281 : x ; x = 564.

The theoretical molecular weight of the hydrated salt, or rather salt containing water of crystallization, is 533.

The theoretical amount of barium called for in the anhydrous salt is 26.6 per cent.

The theoretical amount of barium in the hydrated salt is 25.7 per cent.

The amount of water of crystallization found is 2.88 per cent. ; therefore,

2.88 ÷ 18 :: 0.16 mol. H$_2$O.

That is to say, that 100 parts of barium salt contain 0.16 mol. H$_2$O of crystallization ; therefore 548 parts of barium salt will
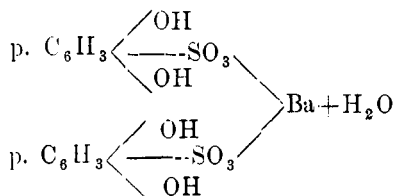
contain $100 : 0.16 = 548 : 4 ; 4 = 0.87$ mol. H_2O, or in round numbers 1 mol. H_2O. We have therefore found :

Barium	24.26	per cent.
Water of crystallization	2.88	"
Molecular weight	564	

Whereas theory calls for

Barium	25.7	per cent.
Water	3.40	
Mol. weight	533	

The formula of the barium salt is therefore, without much doubt :

$$\text{p. } C_6H_3 \begin{cases} OH \\ \text{-----SO}_3 \\ OH \end{cases} \\ \text{p. } C_6H_3 \begin{cases} OH \\ \text{-----SO}_3 \\ OH \end{cases} \Bigg\rangle Ba + H_2O$$

The barium salt is readily soluble in cold water and dilute alcohol and insoluble in strong alcohol. It crystallizes from dilute alcohol in white, six-sided prisms. On adding ferric chloride to its aqueous solution. a momentary deep blue coloration is obtained. which, almost immediately, changes into a dirty yellow color.

POTASSIUM SALT.

This salt was obtained from the barium salt, by decomposing the latter with the theoretical amount of potassium carbonate. On rapidly concentrating the aqueous solution of the same, out of contact with the air as much as possible, it is obtained in the shape of little, yellowish white needles. Better results, however, are obtained by adding three or four volumes of alcohol to the concentrated aqueous solution, and then allowing the mixture to evaporate under the bell jar of an air pump. It is readily soluble in water.

FREE ACID.

$$\text{p. } C_6H_3 - \left(H \ SO_3 \right) \begin{cases} OH \\ OH \end{cases}$$
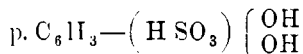
The free acid may be obtained from the barium salt by accurately decomposing the latter with dilute sulphuric acid, filtering

off the $BaSO_4$, shaking up the filtrate with ether, and then distilling off the latter and allowing to crystallize. A simpler method, and one that works very well, is to place the cake resulting from the action of H_2SO_4 upon the hydrochinon, upon porous tiles, till the greater part of the excess of sulphuric acid has been absorbed. Then press the mass between filter paper until nearly every trace of H_2SO_4 has been removed. The mass thus obtained is dissolved in as little alcohol as possible, and set aside to crystallize under the air pump. The free acid is thus obtained in long, well defined brownish, transparent, rhombic prisms (some of the crystals were over 1 cm. long), containing alcohol of crystallization. When exposed over sulphuric acid it effloresces, giving off a part, or all, of its alcohol of crystallization.

0.1155 grm. snb. over H_2SO_4 lost. .0087 grm. alcohol=753 per cent. On now heating to 120° C. the said free acid lost .004 grm. more of alcohol. It will therefore be seen that the larger part of the alcohol of crystallization is lost over H_2SO_4.

The total amount of alcohol lost is therefore .0087+.004=.0127 gram.=10.9 per cent.

This equals 0.43 molecule, or in round numbers one-half molecule alcohol of crystallization.

Theory for $C_6H_3(HSO_3)(OH)_2$. One-half C_2H_6O calls for alcohol 10.7 per cent.

It begins to fuse at 98° c. and is completely fused at 104° c. (uncorrected). Dissolves readily in water and alcohol.

REDUCING ACTION UPON THE HALOID SALTS OF SILVER.

It was thought that the best way to test this question would be to submit some exposed gelatine dry plates to the action of the hydrochinon mono-sulpho acid. For this purpose a preliminary test was made, using an Eatman lantern slide plate, and a solution of the barium salt of the hydrochinon sulpho acid, made slightly alkaline with sodium carbonate. A positive of very fair quality was thus obtained, the tone of color being reddish brown. It developed up very slowly, however, but it is expected that better results will be obtained when using a developer of definite composition.

In conclusion I would state, that I hope soon to complete experiments upon this subject, and will then submit such further results as I may have obtained.