XI.—*On a certain Reaction of Quinine.*

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IN the course of two papers on optical subjects, published in the Philosophical Transactions, I have mentioned a peculiar reaction of quinine having relation to its fluorescence.* About that time I followed out the subject further, and obtained results which were interesting to myself, especially in relation to a classification of acids which they seemed to afford. Not being a chemist, I did not venture to lay the results before the chemical world. I have, however, recently been encouraged by a chemical friend to think that a further statement of the results might prove of some interest to chemists.

The reaction is best observed by diffused daylight entering a darkened room† through a hole in the shutter, which may be

* Phil. Trans. for 1852, p. 541, and for 1853, p. 394.

† In default of a darkened room, a common box, such as an old packing-case, may be readily altered so as to answer very well. The box is sawn obliquely across, the cutting plane being parallel to one edge, as indicated by the figure, which denotes a vertical section. The aperture thus made is covered by a board nailed on, containing a hole, H, destined to be covered by the glass plate, which is kept from slipping down by a small ledge, L. A portion of the upper covering of the box at E is removed to allow the observer to see and mani-

four or five inches square, and which is covered with a deep violet glass, coloured by manganese.* In front of the hole is placed a white porcelain tablet, or else one of the porcelain slabs with shallow depressions used for colour tests. A solution of quinine in very weak alcohol is strong enough for the observations, or else very minute fragments may be used. In some cases, as for example with valerianic or benzoic acid, the presence of alcohol interferes with the reaction.

It will conduce to brevity and clearness to describe in the first instance, in a little detail, the phenomena exhibited by two particular acids, say sulphuric and hydrochloric.

Let a series of drops of the quinine solution be deposited on the porcelain. If one of these be touched by a rod dipped in dilute sulphuric acid, the beautiful fluorescence of the quinine is instantly developed. If another drop be similarly touched by a rod moistened with dilute hydrochloric acid, no apparent effect is produced.† Nor is this all. If a little hydrochloric acid be introduced by a moistened rod into the fluorescing drop, the fluorescence is immediately destroyed. If a little of the sulphuric acid be introduced into the drop containing only hydrochloric acid, no effect is produced.‡

If a series of drops of a solution of quinine in dilute sulphuric acid be deposited, and a little solution of chloride of potassium, sodium, or ammonium be added, the fluorescence is immediately

pulate. In observing, the box is placed near a window, with its slant side turned towards the light; the hole is covered with its glass; the object is placed at O; and the observer looks in through E, covering his head with a dark cloth, to exclude stray light.

* Flint glasses answer best, the colour given by manganese to crown glass being generally somewhat brownish. I have, however, seen one specimen of crown glass coloured by manganese, the colour of which was as fine a purple as that of the flint glasses.

† It is true that a solution of quinine in dilute hydrochloric acid is fluorescent, and with concentrated sunlight, or with sunlight uncondensed, but analysed by absorption or dispersion, the fluorescence comes out strongly. It is, however, notably inferior to that produced by sulphuric acid; and for our immediate object a mode of observation in which it hardly, if at all, appears, is even better than one adapted to bring out comparatively feeble degrees of fluorescence. When I speak in the text of fluorescence being *destroyed*, the expression must be understood in this qualified sense.

‡ It must be understood that I am not here dealing with concentrated acids, nor with any very great preponderance of one kind over another. I suppose all the solutions to be dilute, and the quantity of acid employed, of whatever kind, to be many times that merely required to combine with the quinine.

destroyed. The action of sulphate of potassium, &c., on a solution of quinine in water acidulated, whether with hydrochloric or sulphuric acid, is in each case merely negative.†

Now, on trying a variety of acids, I found that with hardly an exception, unless when the acid character of the acid was only indistinct, the acids ranged themselves with perfect definiteness into two classes, which I will call class A and class B. Those of class A developed fluorescence in a solution of quinine in water just like sulphuric acid, the amount of fluorescence being comparable with that produced with sulphuric acid, and the tint the same. Those of class B not only did not produce it, but destroyed it when produced by acids of the class A. This destruction is produced by the alkaline salts of the acids, as well as by the free acids themselves, and thus we are able to classify acids without having specimens of the free acids at hand.

In the following lists, those acids which were tried only indirectly, by means of one or more of their alkaline salts, are distinguished by an asterisk:—

Class A.	Class B.
Acetic	Hydriodic*
Arsenic	Hydrobromic*
Benzoic	Hydrochloric
Chloric	Hydroferrocyanic*
Citric	Hydropalladiocyanic*
Formic	Hydroplatinocyanic*
Hyposulphuric*	Hydrosulphocyanic*
Iodic	Hyposulphurous*
Malic	
Nitric	
Oxalic	
Perchloric	
Phosphoric	
Silico-fluoric	
Succinic	
Sulphuric	
Tartaric	
Valerianic	

† See the preceding note.

Unless a quinine solution be sufficiently dilute, when alcohol is used, iodic acid produces a precipitate. In what precedes, it must be understood that I refer in all cases to solutions. The character of the fluorescence of the salts of quinine in the solid state varies from salt to salt. The solid iodate obtained by precipitation is strongly fluorescent, with a blue considerably deeper than that of the solutions.

It is not in all cases possible to try all the reactions stated to belong to the acids above mentioned. Thus, in the case of iodic acid, the solution cannot be tested by ferrocyanide of potassium, which instantly decomposes the iodic acid. But the strong fluorescence of the iodic solution, and the immediate destruction of the fluorescence by chloride of sodium, &c., alone suffice to show definitely to which class iodic acid belongs.

The absorption of the fluorogenic* rays by the yellow ferrocyanide of potassium, would itself alone account for the apparent destruction of the fluorescence *if the salt were present in sufficient quantity*. Actually, however, the quantity which suffices to destroy the fluorescence is much less than what would be required to prevent its exhibition by the absorption either of the fluorogenic or of the fluorescent rays, or of both. When the experiment is properly tried, there cannot be a moment's hesitation that the removal of the fluorescence is a true chemical reaction, and not a mere optical effect. This may be further proved by spreading a comparatively large quantity of the ferrocyanide solution in the form of a broad drop on glass, and holding it immediately over the gleaming drop of the quinine solution, when, though the fluorogenic rays entering, and the fluorescent rays leaving the drop, have both to pass through the whole thickness of the absorbing solution, the fluorescence observed is only somewhat reduced. The absorption of the fluorescent rays in this case goes indeed for little; it is the absorption of the fluorogenic rays that we have to consider. That there is a real reaction, and not a mere optical effect, I have further proved by experiments in a pure spectrum, which it would take too long to describe.

* By this term I merely mean rays considered in their capacity of producing fluorescence: the introduction of such a term prevents circumlocution. It is convenient also to have a name for the rays emitted by a fluorescent body. If these be called, as they are a little further on, *fluorescent*, no confusion can practically result, though the term has of course a totally different signification as applied to the rays or to the body emitting them.

Hyposulphurous acid is, it is true, rather easily decomposed, but the destruction of fluorescence by hyposulphite of soda is quite independent of this circumstance. It takes place, for instance, at once on introducing a very dilute solution of hyposulphite of soda into a drop in which the fluorescence had been excited by very dilute citric or acetic acid.

After these remarks, which were necessary to prevent possible misconception, we may return to our lists. A glance at these lists shows that the classification made by the quinine reaction agrees almost exactly with the old distinction of ox-acids and hydracids. There is, however, one acid, the hypsulphurous, which in the quinine reaction ranges itself with perfect definiteness in class B, but which is not, I believe, usually ranked by chemists with the hydracids, except in so far as acids in general have been regarded from this point of view. This led me to seek whether there might not be other analogies between hypsulphurous acid and the hydracids. I have noticed the two following:—

1. It is known that a solution of chloride of mercury reddens litmus, but the blue colour is restored by an alkaline chloride, though itself neutral to colour tests. Now the very same effect is produced by hyposulphite of soda. This salt and chloride of mercury very readily decompose each other; but if very dilute solutions be used, the solution of chloride of mercury having been coloured by a little litmus, it is easy to observe that the *first* effect of the introduction of the hyposulphite, an effect which takes place immediately, prior to the formation of any precipitate, is to restore the blue colour.

2. It is known that cyanide of mercury is hardly decomposed by ox-acids, so as simply to displace the hydrocyanic acid, but readily by hydracids. Now, if a solution of hyposulphite of soda be added to one of cyanide of mercury, the smell of hydrocyanic acid is immediately perceived.

These circumstances bear out, as to hypsulphurous acid, the classification afforded by the quinine reaction. If there be a real difference of constitution between say sulphuric and hydrochloric acids, expressed in symbols by writing the former (according to the old equivalents) $\text{SO}_3 \cdot \text{HO}$, and not $\text{SO}_4 \cdot \text{H}$, and in words by calling it an ox-acid, the mere fact that the radical of hypsulphurous acid, regarded as a hydracid, contains oxygen, does not, of course, oblige us to regard it as an ox-acid. It is

that difference of constitution, whatever it may be, which must decide, and if we may trust the quinine reaction, the isolation of S_2O_3 , the analogue of chlorine, would seem to be less improbable than that of S_2O_2 , the analogue of sulphuric anhydride.

With hydrocyanic and hydrofluoric acids the reaction seemed doubtful. These acids seemed to belong to class B as regards the feeble amount of fluorescence which they developed, but not to prevent the development of strong fluorescence by acetic, sulphuric, &c., acids. Ferridcyanide of potassium had certainly no such action as chloride of sodium, or even ferrocyanide of potassium, in destroying the fluorescence; but the deep colour of the salt prevented a satisfactory decision whether the acid really belonged to class A, or resembled hydrocyanic acid in its action on quinine.

The destruction of the fluorescence of a solution of quinine in a dilute ox-acid on the introduction of a hydracid or its salt, would seem to indicate that the quinine combined by preference with the hydracid. It seemed to me that it would be interesting to restore, if possible, the fluorescence, without precipitation, by the introduction of a substance which should have a preferential affinity for the hydracid. In the case of hydrochloric acid, this may be effected by a salt such as the sulphate or nitrate of the red oxide of mercury. In trying the experiment it is convenient to use only a little hydrochloric acid, or chloride of sodium, &c., otherwise the sparingly soluble chloride of mercury and quinine is precipitated, which, however, redissolves on the addition of more of the mercuric salt. That the restoration of fluorescence is not a mere effect of the acid introduced with the mercuric salt, may be proved by varying the experiment. Let quinine be dissolved with more nitric or sulphuric acid than would otherwise have been necessary; add a little hydrochloric acid so as barely to destroy the fluorescence, and then introduce a little precipitate of oxide of mercury, stirring it up. As the oxide dissolves the fluorescence returns.

Chloride of mercury does not impair the fluorescence of a solution of quinine in an ox-acid; if anything it sometimes seems slightly to increase it. Chloride of barium, strontium, calcium, magnesium, manganese, or zinc, acts like chloride of sodium. The fluorescence destroyed by a chloride is in some measure restored by nitrate of cadmium.

When the fluorescence is destroyed by bromide or iodide of

potassium, it may be restored by oxide of mercury, just as in the case of an alkaline chloride, and under the same conditions.

The precipitate of chloride of mercury and quinine, which is liable to be produced in trying the above reactions, is strongly fluorescent, with a blue which seems to be a trifle greener than that of the solutions. The corresponding precipitate which may be obtained with bromide of potassium, doubtless a bromide of mercury and quinine, is white, and shows a pretty strong orange fluorescence, a very unusual colour for the fluorescence of a white substance. The iodide is pale yellow, and not sensibly fluorescent, at least as examined by daylight with coloured glasses.

At the conclusion of this paper, Dr. Odling made the following observations respecting the constitution of hyposulphurous acid:—

Sodium hyposulphite is usually represented by the formula $\text{Na}_2\text{S}_2\text{O}_3$, together with a molecule of water; and this molecule of water is essential, not only to the hyposulphite of sodium, but likewise to all the hyposulphites, such as the hyposulphite of barium, the double hyposulphite of silver and sodium, and the double hyposulphite of gold and sodium. If, now, instead of writing the formula of the sodium salt, as above, we put it all together in the form $\text{Na}_2\text{H}_2\text{S}_2\text{O}_4$, we have a formula which admits of being halved, and may accordingly be supposed to represent a double molecule of the sodium salt. If this be the case, the single molecule will be NaHSO_2 , corresponding to an acid H_2SO_2 .

Regarded in this manner, hyposulphurous acid forms the first term of a series whose two following terms are sulphurous acid, H_2SO_3 , and sulphuric acid, H_2SO_4 , with this difference, however, that in the two latter acids both the atoms of hydrogen are replaceable by metals, whereas in hyposulphurous acid only one hydrogen atom is thus replaceable, just as in formic acid, H_2CO_2 , which, as pointed out a few years ago by Dr. A. Dupré, may be regarded as the carbon analogue of hyposulphurous acid.

But though hyposulphurous and formic acids may be analogous, so far as their empirical composition is concerned, it by no means follows that they are analogous so far as regards their internal molecular arrangement. Formic acid is well recog-

nized by its properties to be an oxacid, that is to say an acid in which the basic hydrogen is directly combined with oxygen. With regard to hyposulphurous acid, our knowledge is far less complete; but it is quite conceivable that this acid may be a hydracid, that is to say, an acid in which the basic hydrogen is connected with oxygen (if present), not directly, but only through the medium of other elements. The difference of constitution between these two classes of acids may be illustrated by the following examples:—

Hydracids.	Oxacids.
Hydrochloric, HCl.	HOCl, hypochlorous.
Hydrocyanic, HCN.	HOCN, cyanic.
Nitrous, HNO_2 .	HONO ₂ , nitric.

Nitrous acid cannot indeed be placed with certainty among the hydracids, but considering the great number of cases in which NO_2 is capable of taking the place of chlorine or of cyanogen, it is by no means improbable that nitrous acid may be analogous in constitution to hydrochloric and hydrocyanic acids.

The three acids of sulphur above mentioned may be formulated thus:—

$\begin{array}{c} \text{H} \\ \text{H} \end{array} \} \text{SO}_2$	$\begin{array}{c} \text{HO} \\ \text{H} \end{array} \} \text{SO}_2$	$\begin{array}{c} \text{HO} \\ \text{HO} \end{array} \} \text{SO}_2$
Hyposulphurous.	Sulphurous.	Sulphuric.

sulphuric acid being an oxacid, hyposulphurous acid a hydracid, and sulphurous acid an intermediate acid or hydroxacid. With regard to the analogy of fact between the hyposulphites and the halogen salts, the hyposulphites certainly correspond with the latter in their remarkable tendency to form double salts, the constitution of which is not satisfactorily accounted for—analogueous, for example, to the chlorides of mercury and sodium, or of mercury and ammonium. These are double salts, the constitution of which cannot be accounted for according to the commonly received notions of atomicity, unless, indeed, we follow Mr. Wanklyn in assigning to the alkali-metals, a higher atomicity than is generally accorded to them.