



XXXVI. On the prussic and prussous acids

Mr. R. Porrett

To cite this article: Mr. R. Porrett (1810) XXXVI. On the prussic and prussous acids , Philosophical Magazine Series 1, 36:149, 196-204, DOI: [10.1080/14786441008563170](https://doi.org/10.1080/14786441008563170)

To link to this article: <http://dx.doi.org/10.1080/14786441008563170>



Published online: 18 May 2009.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)

at first that I had thus produced the conversion of the mucous acid either into malic acid or tartarous acid; but the experiments which I made to verify this opinion, do not yet appear sufficient to permit me to venture an opinion on the nature of the change which takes place in the experiment which I have described.

XXXVI. *On the Prussic and Prussous Acids.* By Mr. R. PORRETT, *Junior, of the Tower.**

CONSIDERABLE differences of opinion exist among the most celebrated chemists respecting the composition of the prussic acid; some agreeing with Fourcroy and Vauquelin, that oxygen is one of its component parts, and others with Berthollet and Proust, who dispute its presence. Mr. Proust, in his history of the prussiates, asserts, "That there is no fact that indicates oxygen to make a part of this acid, and that from the well-known affinities of its three elements, added to the circumstances under which it is formed, it can scarcely be thought that it does." This difference of opinion implies a want of some decisive experiments, which may set the question for ever at rest; and those which I am going to relate I am induced to think are of that description.

Some time back, I proposed to myself the discovery of a method of preparing a triple prussiate of potash, in a pure state, which should be free from the objections to which the processes in general use are subject. In reflecting on the means most likely to attain this end, it occurred to me, that I should succeed if I decomposed prussiate of iron by double elective attraction rather than by single, employing, instead of a pure potash, that alkali, in combination with a substance uniting the properties of solubility when combined with potash, strong attraction for oxide of iron, and insolubility when united to that oxide. The only substances I could think of possessing all these requisite properties were the succinic acid and sulphur; as the high price of the former precluded its use for this purpose, I determined to employ the latter. I therefore took one ounce of dry sulphuret of potash, and one ounce and a half of the best prussian blue, previously well washed and powdered, and put them into a Florence flask, two thirds

* From *Transactions of the Society for the Encouragement of Arts, Manufactures, and Commerce*, vol. xxvii.—The Society voted their silver medal to Mr. Porrett for this communication.

filled with distilled water ; a disengagement of sulphuretted hydrogen, of ammonia, and of caloric immediately took place. The materials were boiled slowly together for three hours, occasionally replacing the water which evaporated. The whole was then thrown on a filter ; what remained on the filter was black, and consisted of sulphuret of iron and undecomposed prussiate of iron. The liquid that passed through, I found on trial to consist of triple prussiate of potash, and hydroguretted sulphuret of potash. In order to complete the decomposition of the latter, I boiled the liquid again, for the same time as before, with another half ounce of prussian blue, and when cold filtered it. The filtered liquid (A) was now nearly colourless, and free from hydroguretted sulphuret. On pouring a little of it into a solution of oxy-sulphate of iron, I was very much surprised to find that solution changed to a deep blood-red colour, without any precipitate ensuing, instead of forming with it a precipitate of blue prussiate of iron. So unexpected a phenomenon determined me to undertake an examination of this liquid ; with this view I subjected it to the action of the chemical agents mentioned in the following table.

TABLE I. with Liquid A.

Chemical Agents.	Effects.
Paper stained with } turmeric }	No change of colour.
Paper stained with } litmus }	Do. Do.
Potash	{ No disengagement of ammonia, nor any apparent change.
Lime	Do. Do.
Diluted sulphuric acid	{ An expulsion of sulphurous acid ; the liquid becomes slightly opalescent.
Nitric acid (pure) . . .	{ The acid assumes a red colour, but this effect is not permanent.
Oxy-muriatic acid . . .	This acid loses its smell.
Muriatic acid (pure) .	No change.
Muriate barytes	A white precipitate.
Tincture of galls . . .	No change.
Nitro-muriate platina	{ A heavy brilliant ochre, yellow precipitate.
	N 3 Muriate

TABLE I.—(Continued.)

Chemical Agents.	Effects.
Muriate gold	Dark olive brown precipitate.
Nitrate silver	{ A precipitate at first white, but quickly passing to yellow, red, and lastly to brown.
Sulphate silver	{ A dull white or stone-coloured precipitate.
Oxy-nitrate mercury .	A white precipitate.
Oxy-nitrate lead	A white precipitate.
Supersulphate copper	A dull white precipitate.
Muriate bismuth	No precipitate.
Sulphate iron	No change.
Oxy-sulphate iron . . .	{ The solution assumes a deep blood-red colour. No precipitate.

The effects of the sulphuric acid and of the muriate barytes clearly proved the existence of sulphite of potash in the liquid, while that of the oxy-sulphate of iron indicated the presence of some other principle to which the liquid was indebted for its peculiar characters; the separation of this principle in a pure state became therefore a necessary preliminary operation to its examination: after a few trials I succeeded in effecting this separation. The following is the process I employed.

The liquid was evaporated by a gentle heat to dryness; upon the saline residuum alcohol was poured till it ceased to extract any thing: by this means the whole of the sulphite and sulphate of potash was left behind, and the alcohol when filtered held in solution that part only which had the red tingeing property with solutions of iron. The alcohol was now got rid of by distillation, and the salt it left in the retort was redissolved in water. This solution (B) gave the following results with the different metallic solutions.

TABLE II. with Liquid B.

Metallic Solutions.	Effects.
Nitro-muriate platina	{ A precipitate similar to that in Table I. but in a smaller quantity, and longer in forming.
Muriate gold	{ Light olive precipitate, some gold reduced.

Nitrate

TABLE II.—(Continued.)

Metallic Solutions.	Effects.
Nitrate silver	{ A grayish white precipitate, not changing colour.
Sulphate silver	
Nitrate mercury	A copious white precipitate.
Oxy-nitrate mercury .	A white precip. in small quantity.
Nitrate lead	No precipitate.
Oxy-nitrate lead	No precipitate.
Superacetate lead	No precipitate.
Hyperoxymuriate lead	A slight white precipitate.
Supersulphate copper	A dull white precipitate.
Muriate tin	No precipitate.
Muriate bismuth	No precipitate.
Sulphate iron	No change.
Oxy-sulphate iron ...	Same as Table I.
Oxy-sulphate man- } ganese	{ The crimson colour disappears; no precipitate.
Sulphate zinc	
Nitro-muriate cobalt .	No precipitate.
Nitrate nickel	No change.

It is necessary to remark, that in the preceding table, as well as in Table I, several of the nitrates and muriates were slightly reddened, though not in a degree to be compared with the oxy-sulphate of iron. I have not noticed this in the table, because I am not certain whether this effect was not owing to a minute portion of oxide of iron which might have been introduced into those solutions by the acids employed to make them, as both the nitric and muriatic acids of commerce generally contain some; an excess of nitric acid, even if pure, might also cause this effect, as Table I. may convince us. The solutions with which this effect occurred to me were those of bismuth, silver, mercury, lead, cobalt, gold, and platina.

The liquid B is not altered by exposure to the air.

Its effect on oxy-sulphate of iron is the same, whether this sulphate is neutral, or contains an excess of acid, or is supersaturated with carbonate of ammonia.

Sulphuric acid destroys the colour produced on oxy-sulphate of iron, provided the three liquids are in a concentrated state. If there is much water present, no change ensues.

Having obtained the tingeing principle B, separate from
N 4 the

the other salts with which it was contaminated, I asked myself to what were its formation and the simultaneous disappearance of the prussic acid, during the second ebullition, owing? I could imagine but five causes for this that were likely to have been efficient, concerning each of which I made a question to be resolved by experiment, viz.

Question I. Was it owing to the complete separation of the oxide of iron from the triple of prussiate by the sulphur, and the subsequent decomposition of the simple prussiate by the heat of ebullition long continued?

Question II. Was it owing to the action of the sulphurous acid produced?

Question III. Was it owing to the action of the sulphuretted hydrogen?

Question IV. Was it owing to a combination of the prussiate of potash and sulphur?

Question V. Was it owing to the de-oxidation of the prussic acid, by the hydroguretted sulphuret?

To answer the first question, it is only necessary to attend to the results afforded by long-continued boiling of the simple prussiate of potash. I shall state these results as I find them recorded by professor Proust.

They are carbonate of ammonia, carbonate of potash, and some simple prussiate that escapes decomposition, even after four or five successive distillations: there is, therefore, no analogy between the products of this experiment and the liquid A; for, had the latter contained carbonate of potash, it must have changed turmeric paper brown; had it contained carbonate of ammonia, it must have done the same, and likewise have given out ammoniacal gas when potash and lime were added; it must also have turned blue the solution of copper; and had it contained prussiate of potash, it must have produced prussiate of iron when added to the green sulphate of that metal: it will be seen by referring to Table I. that none of these effects were produced. Were further evidence necessary of the dissimilarity of the two liquids, it might be mentioned that professor Proust poured alcohol on the saline residuum of his distillation of the prussiate, which took up a part that he found to be prussiate of potash: had any of the tingeing salt B been present, the alcohol must have dissolved that likewise, and it could not have escaped his observation. We have, therefore, ample grounds for negating the first question.

In order to answer the second question, I passed sulphurous acid gas for a long time through a solution of triple prussiate of potash; the prussic acid was expelled, and sulphite

sulphite of potash formed; but this sulphite was not mixed with any tingeing salt. On the supposition that the disappearance of the prussic acid, in the liquid A, might have been owing to its having been expelled entirely by the sulphurous acid, and that the tingeing liquid resulted from the mutual action of the other principles, namely, the oxide of iron and hydroguretted sulphuret of potash; I subjected a mixture of these materials to long boiling, but could not by this means produce a liquid that tinted oxy-sulphate of iron red. Sulphurous acid gas, passed through water in which prussian blue was diffused, did not in the least affect that compound. These experiments completely refute the opinion on which the second question was grounded.

To enable me to reply to the third question, I passed sulphuretted hydrogen gas for several hours through a solution of triple prussiate of potash, on which it was found to have no effect.

We shall be little disposed to allow that there is any foundation for the fourth question, when we consider the circumstances of the last-mentioned experiment, in which sulphur in the state of the most minute division was offered to the triple prussiate, without any combination ensuing; and also when we compare the effects of the metallic solutions in Table II. with those which would ensue with liquids containing sulphur. But, if any doubt should still be entertained on this subject, the following experiment will perhaps remove it: Into a solution of prussiate of mercury throw some pieces of phosphuret of lime, the oxide of mercury of this prussiate will thus be reduced and separated from the liquid which is to be filtered; some of this liquid poured into carbonate of iron turns it red, the red colour soon disappears, and a white precipitate begins to form; this white precipitate soon changes to green, and if a little nitric or oxy-muriatic acid be now poured upon it, it becomes a perfect blue prussiate of iron. This experiment, in which a liquid turning a solution of iron red was produced without the employment of a particle of sulphur, goes very far to negative our fourth question; and when considered in conjunction with the preceding ones, we can hardly do otherwise than dissent from the supposition which gave rise to that question.

But if the experiment last adduced tends to refute the fourth question, it very strongly supports the fifth; for the changes of colour observable were undoubtedly owing to successive stages of oxidation by the contact of the atmosphere. In confirmation of this question, it may likewise
be

be asserted, that the long boiling with the hydroguretted sulphuret is a powerful de-oxidating process. But it will be said to me, If it is really true that the prussic acid has been de-oxidated by this process, you ought to be able to recompose that acid from the solution B by oxidation. This struck me very forcibly; and being anxious to give this last proof of the truth of my deductions, I attempted the recombination of this acid by several oxidating processes for some time without success: I had at last, however, the particular satisfaction of succeeding completely by the agency of nascent hyper-oxy muriatic acid. The method I employed was the following:

A little hyper-oxy muriate of potash was put into the bottom of a glass tube. Over this some of the liquid B mixed with a few drops of diluted sulphuric acid was poured. The heat of a candle was then applied to the bottom of the tube; and as soon as a violent action commenced, the heat was withdrawn: by this process the prussic acid was reproduced, and was proved beyond the possibility of a doubt by the formation of blue prussiate of iron, when poured into a mixture of green and red sulphate of that metal. Blue prussiate may also be produced at once, by substituting for the diluted sulphuric acid, a solution of green sulphate of iron, with excess of acid.

Having thus succeeded in proving that the tingeing principle of the liquid B was sub-oxidized prussic acid, my next object was to obtain that principle in a free state: for we must recollect that we have hitherto considered it only in combination with potash, with which it formed a neutral salt; this circumstance gave me reason for supposing it an acid, and I therefore determined to attempt its separation by abstracting its base by a stronger acid. The following was the process I employed for the purpose.

The liquid B was evaporated nearly to dryness, and put into a retort with diluted sulphuric acid; a receiver was then adapted to it, and about two-thirds of the liquid distilled over by a gentle heat; what remained in the retort was sulphate of potash. The receiver contained a colourless liquid, with a faint, sour, disagreeable smell, and a decided acid taste. This liquor I have named, in conformity with the principles of the new nomenclature, *prussous acid*, and its salts *prussites*, of which the liquid B contained one in solution, namely the prussite of potash.

The effects of the prussous acid on the earthy and metallic solutions, as far as I have tried them, are noted in the following table.

TABLE

TABLE III. with Prussous Acid.

Chemical Agents.	Effects.
Muriate lime	No change.
Muriate barytes	No change.
Muriate gold	The gold precipitated metallic.
Sulphate silver	Copious white precipitates.
Nitrate silver	
Prussiate mercury	No change.
Nitrate mercury	Copious grayish white precipitate.
Oxy-nitrate mercury	Very slight precipitate white.
Oxy-sulphate iron	{ Solution turns blood-red. No precipitate.
Nitro-muriate platina	
Nitrate lead	No precipitate.
	No change.
	{ Solution becomes red, but hardly any precipitate formed, unless heated, in which case a copious white precipitate ensues. The red colour disappears, a rapid action takes place between the two liquids, and some of the nitric acid of the solution is decomposed.
Oxy-nitrate lead	
Hyper-oxymuriate lead	{ A slight precipitate, probably of muriate of lead.
Super-sulphate copper	
Muriate bismuth	Solution becomes slightly turbid.
Nitrate nickel	
Muriate tin	No precipitates.
Nitrate cobalt	
Sulphate iron	
Sulphate manganese	
Sulphate zinc	

I cannot conclude this part of my memoir without giving a more simple and expeditious process for preparing prussite of potash, than that which I at first discovered. It is the following:

Pour a solution of prussiate of mercury into hydrogu-retted sulphuret of potash, till the mutual decomposition of the two liquids is completed; prussite of potash is instantly formed, and may be separated by filtration from the solid combination of the sulphur and mercury.

I wish

I wish also to observe, that the proportion of prussian blue I have mentioned for boiling with the sulphuret is much larger than is necessary, as I have since succeeded in obtaining prussite of potash when the proportion of prussian blue was only equal to that of the sulphuret, but long boiled with the latter in two distinct and equal portions. The prussite of potash thus obtained is, however, mixed with a much larger quantity of hydroguretted sulphuret than when a greater portion of prussian blue is employed.

Whether the prussous acid can be applied to any use, time and future experiments must decide. It appears to me to be a very delicate test of silver and of iron in solution.

The preceding experiments, by proving the presence of oxygen in prussic acid, give it a stronger claim than it before possessed for being placed among the acids.

The prussous acid possessing stronger acid properties than the prussic is a curious, though not a solitary, instance of the effect of oxygen in diminishing acidity, when its quantity exceeds a certain fixed proportion; in this respect the prussic acid is analogous to the oxy-muriatic.

To recur to the attempt which gave rise to the researches that are the subject of this memoir, I beg leave to state, that I have succeeded in producing pure triple prussiate of potash, by stopping the process before the change which produced the prussite ensued, and by subsequent purification of the lixivium from sulphates and sulphites, by acetate of barytes; from sulphur by acetate of lead; and, lastly, from the acetate of potash thus formed by crystallization; but on account of the complication of this process, I hesitate to recommend it for general use.

Tower, London, April 21, 1809.

ROBERT PORRETT, Jun.

P.S.—It is essential to the success of the experiment, in which the prussic acid is regenerated from the liquid B by the nascently per-oxygenized muriatic acid, that the excess of acid remaining in the liquid, after the oxygenizing process, should be neutralized by an alkali previous to pouring it into the solution of iron, which should likewise be perfectly neutral.

May 8, 1809.

ROBERT PORRETT, Jun.