XXVI. *Some observations on Corrosive Sublimate.* *By* John Davy, *M. D. F. R. S.*

Read June 6, 1822.

I am not aware that the operation of light on corrosive sublimate, has yet been minutely considered. It is known that the *liquor hydrargyri oxymuriatis* of the London Pharmacopœia is decomposed by light; it has been stated, that the compound itself, when exposed to light, undergoes the same change; and it has been recommended, in consequence, to keep it in black bottles.

With a view to acquire some precise information on this subject, the following experiments were instituted.

A few grains of corrosive sublimate, in the state of fine powder, were exposed to sunshine for 14 days in a small glass tube, corked and sealed. No change was then produced, as was proved by the corrosive sublimate dissolving entirely in muriatic acid.

A solution of corrosive sublimate in distilled water was exposed to sunshine for the same length of time. A thin white crust formed, which was found to be calomel; and traces of free muriatic acid were detected in the solution.

Some *liquor hydrargyri oxymuriatis* and solutions of corrosive sublimate in rectified spirit and in ether were exposed to sunshine for the same time. In the former, a considerable crust of calomel formed; whilst in the two latter no change took place.

Some oil of turpentine was poured on corrosive sublimate, and exposed to sunshine for a week. The fluidity of the oil was slightly impaired, but the corrosive sublimate was unaltered.

To a saturated aqueous solution of corrosive sublimate, a few drops of muriatic acid were added, and to another saturated solution, a small quantity of muriate of ammonia. No change was produced in these solutions by the action of light during exposure for three weeks.

From these experiments it may be deduced, that light alone has not the power of decomposing corrosive sublimate, and that it does not produce the effect, excepting when aided by affinities of a complicated nature.

In confirmation of this conclusion, I beg leave to relate some other experiments made with a view to illustrate it, and which, I trust, will not prove uninteresting in themselves.

The solubility of corrosive sublimate in water and alcohol is differently stated by authors. In one experiment, made with as much accuracy as was in my power, 37 grains of distilled water were required to dissolve 2 grains of corrosive sublimate at the temperature 57° FAHRENHEIT, which is in the proportion of about 5.4 per cent. Its degree of solubility increases greatly with the temperature, but in what ratio, it is not easy to ascertain with precision, owing to the trivial circumstances by which the crystallization of the salt is affected.

Alcohol, of specific gravity .816, at 60°, dissolves, I find, half its weight of corrosive sublimate: thus 10 grains of it were completely dissolved in 20 grains of alcohol; one grain more was added and gentle heat applied; it dissolved, but on cooling separated in the form of minute spicular crystals. The saturated solution was of specific gravity 1.08.

Ether, I find, dissolves nearly one-third its weight of corrosive sublimate: thus, 20 grains of sulphuric ether of specific gravity .745, took up 7 grains. It was of the same specific gravity as the alcoholic solution, viz. 1.08. It may be worthy of notice, that the solvent power of ether, as well as I could judge from my experiments, is not increased by elevation of temperature, or diminished by its reduction. The boiling point, too, of the solution and of pure ether, appears to be the same. In the act of ebullition, the solution seems to be decomposed: where a bubble of ether is formed, there a minute portion of corrosive sublimate is precipitated, owing, probably, to the property just mentioned.

Though no change is produced in corrosive sublimate by oil of turpentine under the influence of light, a considerable action and mutual decomposition is the result of a mixture of the two being gently heated. On the application of a gentle heat to corrosive sublimate in fine powder moistened with oil of turpentine, the mixture becomes of a fawn colour; there is a sudden and considerable elevation of temperature, acid fumes are generated, calomel is formed, and if the heat be raised, a residue of carbon is obtained. The results appear to be modified by the proportions of the two substances: when the quantity of corrosive sublimate is large, the whole of the oil appears to be completely decomposed, and the products are, liquid muriatic acid, calomel, and charcoal: when the oil is in excess, the part that escapes decomposition, passes over impregnated with muriatic acid; and, judging from its smell, appears to contain a minute quantity of artificial camphor. From the calomel that is mixed with it, and which rises with it, forming a very dense white vapour, it is not easy, on a small scale of experimenting, to demonstrate the actual formation of camphor.

I believe, that changes very similar take place, when corrosive sublimate is heated with other oils, both volatile and fixed. Of the latter, I have tried one only, oil of almonds; when heated with corrosive sublimate, it immediately blackens, and acid fumes are disengaged. Of the former, I have tried, in addition to the oil of turpentine, the oils of cinnamon, nutmeg, juniper, carraway, peppermint, and cloves. On the application of heat to the first four, mixed with corrosive sublimate, the colour changes to brown, and then to black, and copious acid fumes are disengaged. The mixture of oil of cloves and corrosive sublimate, when gently heated, becomes of a beautiful bright purple, and the heat being raised, acid fumes are disengaged, an oil of the same purple colour distils over, and the residue becomes black. The purple oil appears to be a compound of muriatic acid gas and oil of cloves; and it can be produced either by passing muriatic acid gas into oil of cloves, or by agitating the oil with liquid muriatic acid. On the addition of corrosive sublimate to oil of peppermint, the colour of the oil is immediately changed to bright yellow; on the application of heat, it instantly blackens; a light purple oil volatilises with acid fumes, and calomel with carbonaceous matter remains. The production of a purple oil in this instance, appears to depend on the same cause as in the preceding, and it can be formed in the same way by the action of muriatic acid or its gas.

In a paper published in the Philosophical Transactions for 1812, I have noticed the affinity of muriatic acid for corrosive sublimate. Muriatic acid of specific gravity 1.158, at 74°, dissolves, I find, twice its weight of corrosive sublimate. This solution may be considered as composed of 11 proportions of water, 1 muriatic acid,* and 1 salt. In the act of forming, heat is evolved. At 74° this solution is of specific gravity 2.412. When its temperature is lowered a few degrees, it suddenly becomes solid, and forms a mass of delicate needle crystals, which rapidly melt, when the containing vessel is held in the warm hand.

It is commonly stated in systematic works, that corrosive sublimate is soluble in the sulphuric and nitric acids, as well as in the muriatic acid. From the experiments which I have lately made, this does not appear to be the case. One-tenth of a grain of corrosive sublimate was added to 50 grains of nitric acid of specific gravity 1.45; kept some time at the temperature 90°, it did not diminish in bulk, nor did it appear to dissolve even at the boiling point of the acid, nor did the acid appear turbid on cooling, nor were any crystals deposited. A similar experiment was made with the same quantity of sublimate and 63 grains of concentrated sulphuric acid: at 90° the sublimate did not dissolve; and on the application of heat, fumes appeared, the salt rose through the acid, and a delicate crust of it was formed in the cool part of the vessel.

The experiments which I have made, and which I shall immediately relate, tend to corroborate an opinion long ago

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* New System of Chem. Phil. by JOHN DALTON, vol. ii. p. 295.

entertained, that muriate of ammonia and corrosive sublimate are capable of uniting and of forming a double salt,* and to prove that similar compounds may be formed with some other muriates.

In the dry way, there appears to be an affinity exercised between corrosive sublimate and muriate of ammonia. A mixture of the two, in the proportions of 34 of the former, and 6.75 by weight of the latter, heated, forms a compound more fusible and less volatile than either ingredient separate; it may be kept liquid without volatilising by the gentle heat of a spirit lamp; on cooling, it exhibits a very light grey translucent mass of a faint pearly lustre; strongly heated, it sublimes, and appears to be partially decomposed, as traces of calomel and free muriatic acid are found mixed with the sublimate. This compound, formed of one proportion of each ingredient, has more the character of a chemical compound, than any other mixture of the two ingredients that I have tried.

In the moist way, the affinities of corrosive sublimate and muriate of ammonia are better marked, and some of the combinations of the two have tolerably well defined qualities. The following have the best claim to be considered distinct combinations of any which I have yet made:

No.	Water.	Muriate of Ammonia.	Corrosive Sublimate.
1	9.00 grs.	6.75	34.00
2	9.00	3.37	17.00
3	9.00	3.37	8.50
4	9.00	10.12	25.50

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* The sal-alembroth of the alchemists was a compound of this kind.

No. 1, is liquid at 140°; on cooling, it forms a solid mass of needle crystals. No. 2, is liquid at 85°, and solid at 55°. In the liquid form at the temperature just mentioned, it is of specific gravity 1.98. No. 3, is liquid at 55°, and of specific gravity 1.58. No. 4, is liquid at about 105°; on cooling slowly to 60°, it deposits some crystals which are four-sided prisms, composed of facets alternately broad and narrow.

That corrosive sublimate and muriate of ammonia have a strong affinity for each other, is evident from the circumstance, that united, the solubility of the compound exceeds that of the most soluble ingredient. This is proved by the solubility of the 3d compound just described: farther in proof, it may be mentioned, that a saturated solution of muriate of ammonia at 60°, is capable of dissolving its own weight very nearly of corrosive sublimate, and that after this addition it is capable of taking up more muriate of ammonia; thus, 25.3 grains of such a saturated solution, after having taken up 25.1 grains of corrosive sublimate, dissolved 7 grains more of muriate of ammonia. From this experiment it would appear, that corrosive sublimate is about 17 times more soluble in a saturated solution of muriate of ammonia than in water, and not 30 times, as is stated by some authors.

The results of these experiments led me to make trial of some other muriates, as of baryta, magnesia, potash, and soda.

A saturated solution of muriate of baryta, formed of 20 grains of water and of 8.7 grains of the crystallized salt,* dissolved 16 grains of corrosive sublimate at 60°, and 4 grains

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* 8.7 grains of this salt, heated nearly to redness, lost 1.4 grain water of crystallization.

more when gently heated; on cooling, a very few granular crystals were deposited. The solution was of specific gravity 1.9. After rest for several hours, it deposited a small number of minute and apparently cubical crystals.

31 grains of muriatic acid, of specific gravity 1.58, carefully neutralized with magnesia, dissolved 40 grains of corrosive sublimate, and, when gently heated, 25 grains more. This solution remained transparent on cooling. When 5 grains more of the sublimate were added, these too were dissolved when heated; on cooling, a good many spear-shaped crystals formed. The solution first made, when poured from one vessel into another, had an oily appearance, and was rather less fluid than concentrated sulphuric acid; it was of specific gravity 2.83; gently evaporated, greyish pellicles formed, which rapidly deliquesced on exposure to the air.

A saturated solution of muriate of potash formed of 21 grains of water and 7 grains of dry muriate of potash, gently heated, dissolved 8 grains of corrosive sublimate. On cooling to 60°, it deposited only a very few needle crystals; but when cooled by means of ether to 50°, it became nearly solid, a mass of delicate needle crystals admitting of being inverted.

A saturated solution of common salt, composed of 20 grains of water and 7 of salt, dissolved 32 grains of corrosive sublimate at 60°; gently heated, 3 grains more were dissolved, and remained in solution on cooling; but, on a farther addition of corrosive sublimate, the solution formed by heat, deposited, on cooling, small rhomboidal crystals. The solution, containing 35 grains of sublimate, was of specific gravity 2.14. Like muriate of ammonia, the solubility of common salt in water appears to be increased by combining with corrosive sublimate, but in a less degree.

It appeared probable, that a compound of common salt and corrosive sublimate might be formed in the dry way. 7.5 grains of the former and 34 of the latter were heated together: no proof was afforded of combination having taken place; the corrosive sublimate, on the application of heat, rose as readily as if heated by itself.

I thought it possible that water containing common salt, might have the power of dissolving chlorides that are insoluble in water alone; but experiment did not confirm the conjecture in the instance of calomel and horn silver.

May not the compounds of corrosive sublimate and common salt, muriate of magnesia and baryta, respectively, be considered as constituted of one proportion of each ingredient? The definite nature of the compounds with muriate of ammonia and potash, are perhaps more questionable.

It is worthy of remark, that all these compounds exhibit the properties of the most active constituent, or of that, the saturating power of which is greatest; so that, though the quantity of corrosive sublimate dissolved in any one instance is large, it modifies very little the character of the solution.

To conclude; it would appear from the preceding experiments that these menstrua, which have a strong affinity for corrosive sublimate, prevent its decomposition when exposed to light, as the muriates, alcohol, and ether; and, on the contrary, that those solvents which exercise a weak affinity on it, and have a stronger affinity for muriatic acid, as water, and exceedingly dilute alcohol, aid the decomposing power of light.

The practical application to be deduced, relative to the formula for the *liquor hydrargyri oxymuriatis*, is obvious, and does not require to be pointed out.

Fort Pitt, Chatham,
May 14, 1822.