XXVII.—*On the Precipitation of Solutions of Ammonium Carbonate, Sodium Carbonate, and Ammonium Carbamate by Calcium Chloride.*

By EDWARD DIVERS, M.D.

I HAVE made some experiments on the behaviour of ammonium carbonate with calcium chloride as compared with that of sodium carbonate and of ammonium carbamate with the same substance.

The results of these experiments are principally of interest as supplying a characteristic reaction for the carbamate, and from the evidence they afford of the insufficiency of the commonly received explanation suggested by Kolbe* of the fact first pointed out by Vogel,† that solutions of carbonic anhydride are only imperfectly, or not at all, precipitated in the cold by a mixture of calcium chloride and ammonia. This fact Kolbe considers to be due to the production of some calcium carbamate which remains in solution.

That carbamate is first formed when carbonic anhydride meets ammonia in solution is indeed certain, since as I have recently pointed out, crystallised ammonium carbamate can be readily obtained by acting on ammonia in aqueous solution by carbonic anhydride. But then the behaviour of ammonium carbonate, or even, to a limited extent, of sodium carbonate with the mixed ammonia and calcium chloride I find to be precisely that which in the case of carbonic anhydride is attributed to ammonium carbamate.

If to a mixture of ammonia-water and solution of calcium chloride a very little dilute solution of ammonium carbonate is added with agitation, a gelatinous precipitate forms, and immediately after re-dissolves. On standing, a precipitate more or less gelatinous again forms, but only very gradually, which slowly assumes the chalky condition, particularly if the solution be freely diluted with water. If the calcium chloride and ammonia

* Handwörterbuch der Chemie, vol. i, suppl., p. 157.

† Recherches Analytiques sur le Corail Rouge, Annales de Chimie, vol. lxxxix, p. 113 (1819); Ueber eine unsichere Methode das Verhältniss des Kohlensäure Gases bei Analysen zu bestimmen, Schweigger's Journal für Chemie und Physik, vol. xxxiii, p. 204 (1821).

are added to a larger proportion of ammonium carbonate, but still in marked excess, some of the gelatinous precipitate first formed is permanent, but more precipitate is gradually deposited. It is, with either mixture, days before precipitation is so far complete that the supernatant fluid no longer gives a precipitate on being heated.

The addition of the mixed ammonia and calcium chloride solutions to a very little exceedingly dilute solution of sodium carbonate, throws down a gelatinous precipitate, which redissolves nearly or entirely, and forms a solution which only after some time deposits a chalky precipitate. Added, still in considerable excess, to a larger proportion than in the last case of very dilute solution of sodium carbonate, the mixed reagent causes a permanent, at first gelatinous, afterwards chalky, precipitate, but even in three hours the clear supernatant fluid sometimes yields a good precipitate when heated.

So that the action of sodium carbonate is the same in kind as that of ammonium carbonate and differs only in degree; while the behaviour of the latter salt with the excess of calcium chloride and ammonia is sensibly and practically identical with that of a solution of carbonic anhydride with the same reagents.

As regards the precipitation effected by heat in the mixture of excess of calcium chloride and ammonia with ammonium carbonate, this is only slowly produced if the mixture is strong in ammonia and calcium chloride.

If in the previous experiments the calcium chloride is used unmixed with caustic ammonia, the carbonates of ammonium and of sodium show at first each the same behaviour as before; but even with the ammonium salt the second precipitation of chalky carbonate is now not long in setting in, and after the supernatant fluid has stood about two hours, it fails to give a precipitate when heated, while with the sodium salt the reprecipitation of calcium carbonate takes place almost immediately, and the supernatant solution fails in a very short time to yield a precipitate on boiling.

It therefore appears that caustic ammonia in the presence of excess of calcium chloride very considerably retards the precipitation of calcium carbonate.

Fragments of a cake of ammonium carbamate, obtained by distillation, and almost pure, except superficially, were washed with a little water to remove the outer portions, and dissolved

in cold water so as to form a dilute solution. Some of this solution treated without delay with excess of calcium chloride, gave a slight precipitate at once. In two hours the supernatant fluid gave a very slight precipitate on being heated, but in four hours ceased to give any at all. A solution of ammonium carbonate of about the same strength would have given very much more precipitate at first, and the supernatant fluid would have failed to give when heated any precipitate in two hours or less. Ammonium or calcium carbamate, therefore, very soon passes into the state of carbonate in the presence of calcium chloride when caustic ammonia is absent. The presence of ammonia in addition materially impedes this change. Thus, when the above experiment with the carbamate was repeated with the modification of adding caustic ammonia, no precipitate appeared for hours, and in eight hours only a very slight one, while a day afterwards the clear supernatant fluid gave when heated a very copious precipitate. Other and decisive evidence that ammonia retards the conversion of ammonium carbamate into carbonate, has been given in my paper on the combinations of carbonic anhydride with ammonia and water: further evidence will also be given presently.

When, therefore, a solution of carbonic anhydride is treated with excess of calcium chloride and ammonia, it first forms carbamate which slowly passes into carbonate; but its imperfect precipitation as carbonate is essentially due to the fact that the excess of calcium chloride and ammonia greatly retards the complete precipitation of calcium carbonate in the cold.*

When ammonium or sodium carbonate is added in excess to calcium chloride, the action of ammonia is very different. A moderately strong solution of ammonium carbonate mixed with a very little dilute solution of calcium chloride gives, in the absence of ammonia, a gelatinous precipitate redissolving on agitation, as Storer has particularly pointed out.† This solution, according to my experiments, soon deposits the calcium

* According to Storer (First Outlines of a Dictionary of Chemical Solubilities, 1864, p. 110), carbonic anhydride produces no precipitate with the mixed solution of calcium chloride and ammonia, *even when the mixture is boiled*, in presence of excess of ammonium chloride. This statement I have not been able to confirm. Carbonic anhydride solution, mixed with ammonia and ammonium chloride, gives at once a well-marked precipitate when heated with calcium chloride, whether this has been added in excess, or in quantity insufficient to precipitate it all.

† Op. cit., p. 110.

carbonate in the chalky state, and in less than an hour the filtered solution gives no precipitate when boiled. In the presence of caustic ammonia it becomes almost impossible to add the smallest quantity of calcium chloride without causing an immediate gelatinous precipitate, permanent on agitation, and the mother-liquor soon fails to give a further precipitate on boiling. So that in the presence of ammonium carbonate, ammonia determines the precipitation of calcium carbonate instead of impeding it, as it does in the presence of calcium chloride. The greater insolubility of calcium carbonate in solution of ammonium chloride or nitrate in the presence of ammonium carbonate and ammonia has been pointed out by Fresenius,* and also its much greater insolubility in ammonia-water than in pure water.† His experiments, however, refer to the crystalline precipitated calcium carbonate: the above experiment shows the great insolubility, in the presence of ammonium carbonate and ammonia, of calcium carbonate in its gelatinous and, under other circumstances, much more soluble condition. It is to be plainly inferred from the statements in some of the best works on qualitative analysis that, in the precipitation of calcium salts by ammonium carbonate, ammonia is added merely to ensure the absence of any acid carbonate; but it is evident that the presence of free ammonia is necessary to render the precipitation instant and complete.‡

The reactions of sodium carbonate used in excess, both in the presence and absence of ammonia, are quite similar to those obtained with ammonium carbonate.§

Ammonium carbamate solution when treated with less than its equivalent of calcium chloride, very soon yields a precipitate, and in about two hours the filtered solution gives no further precipitate on being heated. The reaction is therefore the same as when the calcium chloride is added in excess. When ammonia is added, the calcium chloride gives an instantaneous, but slight, precipitate with excess of the solution of the carbamate. The precipitate increases very slowly on standing, and the supernatant solution a day after gives a further copious

* Quantitative Analysis, fourth English edition, p. 107. † Op. cit., p. 164.

‡ Ammonia quickens the precipitation of ammonio-magnesian carbonate.

§ The sodium carbonate used to determine this fact was pure, and was dissolved in cooled, freshly-boiled water, so as to ensure the absence of any acid carbonate, by neutralizing which, it might otherwise be said, the ammonia produced its effect.

precipitate on boiling. The immediate precipitation is undoubtedly due to the presence of ammonium carbonate; and the very slow further precipitation of the solution affords another proof how slowly the carbamate changes into carbonate, in presence of free ammonia.

The distinguishing reaction, therefore, between ammonium carbamate and ammonium carbonate is that, added *in excess* to ammonia and calcium chloride, the carbamate precipitates the calcium very slowly, while the carbonate precipitates it immediately.

The fact that the carbamate gives a more soluble calcium salt than the carbonate does, is of itself hardly of any use as a test, because, firstly, the apparent solubility depends so much on the strength of the solution; and secondly, except in the presence of ammonia, the carbamate so rapidly passes into carbonate.

The gelatinous precipitate (calcium carbamate?) produced in solution of ammonium carbamate by excess of calcium chloride, can be dissolved by sufficient water added immediately. Water also sensibly dissolves a precipitate of gelatinous calcium carbonate, but not at all to the extent that it does the former precipitate. The carbamate precipitate has appeared to me to be less soluble in calcium chloride solution than in pure water, but I cannot speak with much certainty on this point.

Concentrated solutions of ammonium carbonate and sodium carbonate act in a special way with very concentrated solution of calcium chloride. When a concentrated solution of the ammonium salt is treated with a very little saturated solution of calcium chloride and agitated, a precipitate is produced, almost invisible at first, which rapidly subsides in gelatinous flocks; further addition of calcium chloride fills the liquid with the precipitate, but still not so as to gelatinize and solidify the liquid, as it would do were the solutions much less concentrated; when the calcium chloride is added to large excess, the precipitate already formed changes its appearance, becoming white and opaque, and not unlike silver chloride. When to a saturated solution of calcium chloride a drop of saturated, or very concentrated solution of ammonium carbonate is added with agitation, the precipitation is also immediate and scanty, and the precipitate sinks rapidly, but it is in curdy, or rather thready, slightly translucent particles. The form of the precipitate is

probably to be accounted for by the fact that the solutions mix with difficulty. The supernatant fluid, containing the excess of calcium chloride, can easily be decanted from the precipitate, and this can be washed by decantation; by such treatment it undergoes little change in appearance, beyond getting more opaque, and seems to be nothing but calcium carbonate. If the carbonate be added in larger quantity to the calcium solution, a good deal of gelatinous precipitate forms, but not to anything like the extent it would do with more dilute solutions; in fact, by adding water in moderate quantity to the mixture, the whole quickly becomes solid. If the calcium chloride used in the above experiments be first charged with ammonia, the results appear to be the same. A concentrated solution of sodium carbonate substituted for that of ammonium carbonate, gives quite similar results.

The fact that a very concentrated ammoniacal solution of ammonium carbamate gives with a saturated solution of calcium chloride a precipitate which is soluble in water, and which has a composition indicating that it is either calcium carbamate or ammonio-calcium carbonate, has been noticed in my paper on the combinations of carbonic anhydride with ammonia and water.