

386. Researches on Ammines. Part X. Triammines of Bivalent Platinum.

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There are shown to be two classes of platinous triammines. The one class, which includes the chloro-, bromo-, and nitro-triamminoplatinous salts, dissolve in water as such, and are shown by conductivity measurements to behave as salts of univalent kations. Solutions of these compounds also yield *pink* chloroplatinites and acidotriamine picrates. The other class dissolve with complete or substantial conversion into aquo-triammines: $[\text{Pt}(\text{NH}_3)_3\text{X}]\text{X} + \text{H}_2\text{O} = [\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{X}_2$. The nitrate-, sulphato-, and picrato-triammines undergo complete aqutation, and conductivity measurements indicate the presence of salts of bivalent kations. Solutions of these salts yield aquotriamminoplatinous chloroplatinite and picrate, the former being green. Conversion into aquo-salt is partial in the cases of carbonato- and oxalato-triammines.

In $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)]\text{Cl}_2$ the ethylenediamine molecule is shown to be attached to platinum at one point only, so that the platinous atom is still 4-covalent. If one molecule of ammonia is expelled, the ethylenediamine molecule occupies *two* positions in the complex. It is concluded that bivalent platinum has no tendency to exist in the 5-covalent state.

THE acidotriamminoplatinous salts are of particular interest since they constitute the only group of metallic ammines hitherto investigated in which an acid radical forms part of a 4-covalent kation. The existence of two classes of platinous diacido-diammines was demonstrated in Part IX (*J.*, 1938, 1338). Members of the one class, which includes the dichloro-, dinitro-, di-iodo-, and dihydroxo-compounds, dissolve in water unchanged, while the other class, to which the dinitrato-, dipicrato-, and sulphato-diammines belong, dissolve as diaquo-salts, which, however, exist only in solution: $[\text{Pt}(\text{NH}_3)_2\text{X}_2] + 2\text{H}_2\text{O} \rightleftharpoons [\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{X}_2$. It has now been shown that there are similarly two types of platinous acidotriammines. In aqueous solution, the equilibrium $[\text{Pt}(\text{NH}_3)_3\text{X}]\text{Y} + \text{H}_2\text{O} \rightleftharpoons [\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{XY}$ lies almost entirely to the left in the one case and to the right in the other, the behaviour depending on the nature of X. In the former case, the solutions are neutral, while in the latter they contain aquotriamminoplatinous salts, the noticeable acidity of which (less pronounced, however, than that of the corresponding diammines) is due to the hydroxo-aquo-equilibrium: $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{X}_2 \rightleftharpoons [\text{Pt}(\text{NH}_3)_3(\text{OH})]\text{X} + \text{HX}$.

The aquotriamine salts, like the diaquodiammines, usually exist only in solution, the solid compounds which separate from the solutions being the original acidotriammines. The solutions containing acido-triammines give, with a soluble chloroplatinite, pink precipitates of the corresponding chloroplatinites, while those containing aquo-triammines yield a green precipitate of aquotriamminoplatinous chloroplatinite. The two classes also react differently with ammonium picrate, the former reacting with one mol. of picrate to form an acidotriamminoplatinous picrate while the latter yield picratotriamminoplatinous picrate with two mols. of picrate. Evidently aquotriamminoplatinous picrate is unstable in the solid state but is present in the aqueous solution of the picrato-picrate (see Table II).

That chloro-, bromo-, and nitro-triamminoplatinous salts dissolve without aqutation has been demonstrated by measurement of their electrical conductivities, which are of the order required for salts of univalent kations (see Table I). This conclusion was confirmed by precipitation of pink chloroplatinites and preparation of *chloro-, bromo-, and nitro-triamminoplatinous picrates*.

The only information available regarding other acidotriamminoplatinous salts is due to Cleve (*K. Svensk Vet. Akad. Handl.*, 1872, **10**, No. 9), who claimed to have obtained the nitrate $\text{Pt}(\text{NH}_3)_3(\text{NO}_3)_2$ and the sulphate $\text{Pt}(\text{NH}_3)_3\text{SO}_4$ by interaction of chlorotriamminoplatinous chloroplatinite (Cleve's salt) and silver nitrate or sulphate. No details were recorded, and attempts to prepare the salts by this method have proved unsuccessful. Two equivalents of silver salt should react with one molecular proportion of Cleve's salt yielding *chlorotriamminoplatinous nitrate* or sulphate, and this has been verified experimentally in the case of the former salt. When, however, four equivalents of silver salt were used, as required by the equation $[(\text{Pt}(\text{NH}_3)_3\text{Cl})_2\text{PtCl}_4 + 4\text{AgNO}_3 = 2[(\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{NO}_3 + 2\text{AgCl} + \text{Ag}_2\text{PtCl}_4$, the filtrate was not chlorine-free, and this was found to be due to interaction between silver chloroplatinite and silver nitrate (see p. 1914). It was found possible to isolate *nitratotriamminoplatinous nitrate* by carrying out Cleve's preparation in two stages, treating chlorotriamminoplatinous nitrate, prepared as above, with one mol. of silver nitrate, but the compound was more conveniently prepared by treating chlorotriamminoplatinous chloride with silver nitrate. The product is hemi-hydrated so formulation as an aquo-salt is excluded. It dissolved easily in water and the noticeable acidity of the solution suggested that the salt was present in solution, not as

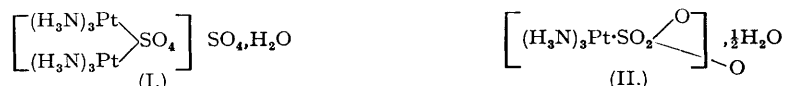
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nitratotriammino-, but as aquotriammino-platinous nitrate. This conclusion was confirmed (a) by preparation from it of aquotriamminoplatinous chloroplatinite (green) and *picratotriamminoplatinous picrate*, (b) by measurement of the electrical conductivity of the solution, which was of the order required for a salt of a bivalent kation (see Table II).

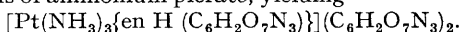
The *sulphato-triammine* was prepared by treating a solution containing aquotriammino-platinous nitrate with excess of sulphuric acid. The product, after drying over phosphoric oxide, contained only half the amount of water required for aquotriamminoplatinous sulphate. It could be formulated alternatively as (I) or (II), the sulphate radical in (II) being attached to



the platinum atom at one point only. A compound of formula (II) would be analogous to the sulphatopentamminocobaltic salts (Jørgensen, *J. pr. Chem.*, 1885, **31**, 262), containing a "bound" sulphate ion, and would be a non-electrolyte if it dissolved without aquation. The aqueous solution, however, was acid to litmus and yielded green aquotriamminoplatinous chloroplatinite when treated with a soluble chloroplatinite. Thus solution had been accompanied by aquation, which might be expected to yield aquotriamminoplatinous sulphate, $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{SO}_4$, whichever formula is adopted for the solid substance. The ease with which aquation occurs favours formula (II). The presence in solution of the aquotriammine salt was confirmed by conductivity measurements (Table II).

Carbonato- and *oxalato-triamminoplatinum* have been obtained by the action of excess of silver carbonate or oxalate on *bromotriamminoplatinous bromide*, and in these cases also formulation of the solid compounds as aquo-salts is excluded, since the former is hemi-hydrated and the latter can be obtained anhydrous. They may be formulated analogously to formulæ (I) and (II) given for the sulphato-triammine. However, it seems unlikely, in view of the strong tendency of the carbonate and the oxalate radical to complex formation, that compounds of structure (I) would undergo aquation. Actually, sufficient aquation occurs for the salts to yield green precipitates with the chloroplatinite ion, though the conductivity data show that this aquation is very incomplete compared with that of the sulphato-triammine. The conductivity data for the oxalato-triammine are so low that formula (I) is definitely excluded.

It has frequently been suggested that in the process of ammine formation, the metals tend to simulate the electronic arrangement of the next inert gas. In the case of the bivalent platinum ion, this would require quinquenevalency (2, 8, 18, 32, 16 \rightarrow 2, 8, 18, 32, 18, 8). As no well-established examples of quinquenevalent platinum have hitherto been described, an attempt was made to prepare such a compound by treating chlorotriamminoplatinous chloride with ethylenediamine. It might be expected that the powerful chelate group present in the molecule of this substance would attach itself directly to the complex, if 5-covalency is possible, yielding ethylenediaminotriamminoplatinous chloride $[\text{Pt}(\text{NH}_3)_3\text{en}]\text{Cl}_2$ (where en = $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$). A compound of this molecular formula has actually been obtained, but it reacted with three molecular proportions of ammonium picrate, yielding



Thus the ethylenediamine molecule is attached to the platinum atom at one point only, and the platinum is still in the 4-covalent state. When $[\text{Pt}(\text{NH}_3)_3\text{en}]\text{Cl}_2$ was titrated with acid or boiled with water, a molecule of ammonia was removed, and the ethylenediamine molecule then occupied two positions in the complex, as was shown by precipitation of $[\text{Pt}(\text{NH}_3)_2\text{en}](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2$ by excess of picrate. These results indicate that there is no tendency for bivalent platinum to exist in the 5-covalent state.

EXPERIMENTAL.

Chlorotriamminoplatinous Chloride.—Using Tschugaev's method (*J.*, 1915, **107**, 1249), difficulty was experienced in obtaining the compound pure. The following modification gave excellent results. 3.5 G. of tetramminoplatinous chloride were boiled for 3 minutes with 9.66 g. of Cleve's salt (8% excess) and 350 ml. of water acidified with hydrochloric acid. After cooling, the green Magnus salt and excess of Cleve's salt were removed and the filtrate was concentrated to small bulk at 50° under reduced pressure. After further filtration from traces of Cleve's salt, the remaining water was removed in a vacuum over sulphuric acid, and the solid product left over soda-lime to remove traces of hydrogen chloride (yield 6.1 g.). If less water or smaller excess of Cleve's salt was used, the product was contaminated with tetrammine.

Chlorotriamminoplatinous Nitrate.—3 G. of Cleve's salt were heated to 70° with 1.132 g. (2 mols.) of silver nitrate and 120 ml. of water. After collection of silver chloroplatinite, the colourless filtrate was concentrated to 30 ml. under reduced pressure at 50°. On addition of alcohol and ether, white, irregular, microscopic plates separated (0.57 g.) (Found: Pt, 56.7; N, 16.5; Cl, 10.0. $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{NO}_3$ requires

Pt, 56.8; N, 16.3; Cl, 10.3%). The compound was easily soluble, giving a neutral solution which gave no immediate precipitate with silver nitrate. The silver chloroplatinite was suspended in water and left overnight in contact with a further 2 mols. of silver nitrate. The filtrate from silver chloride and unchanged chloroplatinite contained only 0.32 mol. of silver nitrate. Chlorotriamminoplatinous nitrate was best prepared by adding 0.5355 g. (1 mol.) of silver nitrate dropwise to a solution of chlorotriamminoplatinous chloride (1 g.). The filtrate was evaporated in a vacuum over sulphuric acid, yielding 0.95 g. of square plates (Found: Pt, 56.6; Cl, 10.2%). The aqueous solution gave a pink precipitate with ammonium chloroplatinite.

Chlorotriamminoplatinous picrate was precipitated as large yellow needles (1.5 g.) on mixing solutions of chlorotriamminoplatinous chloride (1 g.) and ammonium picrate (1.2 mols.) {Found: Pt, 38.4; N, 16.3; Cl, 6.7. $[\text{Pt}(\text{NH}_3)_3\text{Cl}](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 38.3; N, 16.5; Cl, 7.0%}.

Bromotriamminoplatinous bromide does not appear to have been isolated previously, though Tschugaev (*loc. cit.*) obtained the bromoplatinite $[\text{Pt}(\text{NH}_3)_3\text{Br}]_2\text{PtBr}_4$. The salt has now been prepared by converting chlorotriamminoplatinous chloride (2 g.) into aquotriamminoplatinous nitrate in 20 ml. of water (see nitratotriamminoplatinous nitrate below). The ice-cooled product was treated with colourless fuming hydrobromic acid (20 ml.), whereupon an immediate cream precipitate was obtained (1.8 g. of microscopic, acicular aggregates). It was washed successively with alcohol and ether and dried over soda-lime (Found: Pt, 48.2; N, 10.2; Br, 39.4. $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Br}$ requires Pt, 48.1; N, 10.3; Br, 39.4%). 0.636 G. of the salt dissolved in 100 g. of water at 20°. The aqueous solution was neutral to litmus and yielded a pink precipitate with ammonium chloroplatinite.

Bromotriamminoplatinous picrate was obtained as irregular, microscopic, yellow plates when a solution of the bromide was treated with one mol. of ammonium picrate {Found: Pt, 35.2; N, 14.9; Br, 14.2. $[\text{Pt}(\text{NH}_3)_3\text{Br}](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 35.2; N, 15.2; Br, 14.4%}.

Nitrotriamminoplatinous Nitrate.—The very unstable nitrite of this series has been described by Tschugaev (*J.*, 1916, **109**, 1286). The much more stable nitrate has now been prepared. 2 G. of chlorotriamminoplatinous chloride were converted as above into a solution of chlorotriamminoplatinous nitrate. This was shaken for an hour with 0.970 g. (1 mol.) of silver nitrite and left overnight. The neutral, colourless filtrate was evaporated to small bulk in a vacuum over sulphuric acid and treated with excess of alcohol and ether, whereupon a voluminous white product separated (1.3 g. of acicular aggregates, very soluble in water) (Found: Pt, 55.3; N, 20.0; NO_3 , 17.2. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{NO}_3$ requires Pt, 55.1; N, 19.8; NO_3 , 17.5%). (Sunlight should be excluded during precipitation, or some decomposition occurs.) The salt gave a salmon-pink chloroplatinite (microscopic, acicular aggregates).

Nitrotriamminoplatinous picrate was precipitated as slender yellow needles when a solution of the nitrate was treated with one mol. of ammonium picrate {Found: Pt, 37.2; N, 18.6. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 37.5; N, 18.9%}.

Nitratotriamminoplatinous Nitrate.—Cleve (*loc. cit.*, p. 64) claimed to have obtained this compound, in monohydrated form, by double decomposition between Cleve's salt and silver nitrate. Several preparations were made, refluxing with four mols. of silver nitrate, but in no case was the filtrate chlorine-free. The hemihydrated salt was readily obtained pure when chlorotriamminoplatinous chloride (2 g.) was shaken for an hour with 2.142 g. (2 mols.) of silver nitrate and 30 ml. of water. After being left overnight, the product was filtered and the filtrate, which was colourless and acid to litmus, was (a) treated with 400 ml. of alcohol and ether, whereby 1.9 g. of a white micro-crystalline precipitate were obtained (Found: Pt, 51.5; N, 18.8. $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Pt, 51.5; N, 18.5%), or (b) taken to dryness in a vacuum over sulphuric acid, the anhydrous salt then being obtained (Found: Pt, 52.7. Calc.: Pt, 52.7%).

Aquotriamminoplatinous chloroplatinite was obtained as an immediate acicular green precipitate when the aqueous solution of nitratotriamminoplatinous nitrate (*i.e.*, aquotriamminoplatinous nitrate) was treated with ammonium chloroplatinite (Found: Pt, 64.9; N, 7.3. Calc. for $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{PtCl}_4$: Pt, 64.9; N, 7.0%). No loss of weight or change of colour occurred when the compound was left over phosphoric oxide for two weeks. This compound and the corresponding bromoplatinite were described by Tschugaev and Tschernjaeff (*Compt. rend.*, 1915, **161**, 792), and appear to be the only aquotriamines which exist in the solid state.

Picratotriamminoplatinous Picrate.—0.4 G. of chlorotriamminoplatinous chloride was treated as above with 2 mols. of silver nitrate and the resulting solution of aquotriamminoplatinous nitrate was added to 0.636 g. (2.2 mols.) of picric acid which had been converted into the ammonium salt. 0.75 G. of large needles was precipitated {Found: Pt, 28.1; N, 17.6. $[\text{Pt}(\text{NH}_3)_3(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$ requires Pt, 27.8; N, 18.0%}. There was no loss of weight at 100°.

Sulphatotriamminoplatinum could not be obtained by Cleve's method (*loc. cit.*) or by interaction of chlorotriamminoplatinous chloride or bromotriamminoplatinous bromide and silver sulphate. 2 G. of chlorotriamminoplatinous chloride were converted as above into an aqueous solution of aquotriamminoplatinous nitrate, which was concentrated to 25 ml. in a vacuum over sulphuric acid, treated with an equal volume of dilute sulphuric acid, and precipitated with alcohol and ether (120 ml.). The voluminous white microcrystalline product (1.6 g.) was dissolved in the minimum amount of water, and reprecipitated with alcohol and ether. The compound was fairly soluble, giving a slightly acid solution, but considerable heating and shaking were required to dissolve it. The solution yielded a green chloroplatinite. If dried overnight over soda-lime, the compound was monohydrated (Found: Pt, 54.6; N, 11.7; SO_4 , 26.6. $[\text{Pt}(\text{NH}_3)_3(\text{SO}_4)] \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Pt, 54.2; N, 11.7; SO_4 , 26.7%), but if it was left for a week in a vacuum over phosphoric oxide, a hemihydrate was obtained (Found: Pt, 55.6; N, 11.9; SO_4 , 27.2. $[\text{Pt}(\text{NH}_3)_3(\text{SO}_4)] \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Pt, 55.6; N, 12.0; SO_4 , 27.3%).

Carbonatotriamminoplatinum.—3 G. of bromotriamminoplatinous bromide were shaken for 3 hours with silver carbonate freshly precipitated from 12 g. of silver nitrate and suspended in 50 ml. of water. After removal of silver bromide, the filtrate was ice-cooled and precipitated with alcohol and ether. 1.7 G. of very soluble white needles were obtained and dried over magnesium perchlorate (Found: Pt, 61.8; N, 13.6; C, 4.0; H, 3.1. $[\text{Pt}(\text{NH}_3)_3(\text{CO}_3)] \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Pt, 61.9; N, 13.3; C, 3.8; H, 3.2%). The substance yielded a green chloroplatinite.

Electrical Conductivities at 25°.—In the tables, v is the reciprocal of the concentration in g.-mols. per litre and λ is the corrected molecular conductivity in mhos. Measurements in Table I were made (a)

Acido-triammines which dissolved without aquation.

v	32.	64.	128.	256.	512.	1024.	∞
λ for $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}$ $\begin{cases} a \\ b \end{cases}$	100.4	102.6	104.4	106.0	108.8	116.2	—
„ $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{NO}_3$ $\begin{cases} a \\ b \end{cases}$	100.4	103.7	106.5	109.4	117.5	130.5	—
„ $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Br}$ $\begin{cases} a \\ b \end{cases}$	107.1	109.5	111.4	113.0	115.2	117.8	—
„ $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{NO}_3$ $\begin{cases} a \\ b \end{cases}$	107.1	117.8	122.8	134.3	146.6	160.2	—
„ $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Br}$ $\begin{cases} a \\ b \end{cases}$	—	—	109.4	113.0	116.1	118.2	—
„ $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)]\text{NO}_3$	—	—	111.5	116.0	120.0	122.8	—
„ $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)]\text{NO}_3$	101.7	107.3	111.6	115.0	117.9	120.1	125.8

($n = 1.48$)

The values for nitrotri(aminoplatinous) nitrate showed no increase on standing, and the linear λ^{-1}/ν graph showed that no aquation occurred on dilution. This might be expected, since aquation would necessarily be preceded by conversion of the nitro- into the nitrito-triammine; λ_{∞} for this compound was obtained by means of the $1/(\lambda - (c\lambda))^{n-1}$ graph, and gives a value of 54.4 mhos for the mobility of the nitrotri(aminoplatinous) ion at 25°, 71.4 mhos being taken as the mobility of the nitrate ion. The values for nitratotri(aminoplatinous) nitrate showed no increase on standing and indicate immediate and complete aquation to $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})](\text{NO}_3)_2$. They differ but little from the values previously recorded for the *cis*-dinitratodiammine, which has been shown to dissolve as *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (see Part IX, *loc. cit.*). The values recorded for picratotri(aminoplatinous) picrate agree well with the previously recorded value of 182.6 mhos for the *cis*-dipicratodiammine at a dilution of 1024 litres, and indicate complete aquation to aquotri(aminoplatinous) picrate. The data obtained for the sulphotri(aminoplatinous) increased on standing, reaching equilibrium in an hour. In this case, aquation was evidently slower, but conversion into $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{SO}_4$ was fairly complete. The values agree closely with those previously recorded for the *cis*-sulphotodiammine, which has similarly been shown to dissolve as

TABLE II.

Acido-triammines which dissolved with complete or substantial aquation.

ν	64.	128.	256.	512.	1024.
λ for $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{NO}_3$	—	232.1	250.5	259.0	267.0
„ $[\text{Pt}(\text{NH}_3)_3(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)$	—	—	—	178.3	190.4
„ $[\text{Pt}(\text{NH}_3)_3(\text{SO}_4)]$ equilibrium values	—	—	165.4	205.9	229.6
„ $[\text{Pt}(\text{NH}_3)_3(\text{CO}_3)]$	69.1	79.4	86.4	91.3	104.4
„ $[\text{Pt}(\text{NH}_3)_3(\text{C}_2\text{O}_4)]$	42.3	44.6	46.6	48.1	48.9

cis- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{SO}_4$. The conductivities of the carbonatotriammine increased on standing, reaching equilibrium in from 15 to 45 minutes, according to the concentration. At a dilution of 256 litres, this increase amounted to 15% in 25 minutes. Even at the lower concentrations, the equilibrium values indicate less than 50% aquation. In the case of the oxalato-triammine, the increase in conductivity on standing was much less (2% at a dilution of 256 litres) and equilibrium was reached in 20 minutes. Aquation was, however, very incomplete, amounting only to about 20% even at the lower concentrations.

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