and carbohydrazide towards the above reagents, and the possibility of estimating chloric, bromic and iodic acids by means of semicarbazide.

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INDIRECT FORMATION OF DOUBLE SALTS.[1] V. THE DOUBLE PLATINIC, CUPRIC AND SILVER IODIDES OF SUBSTITUTED AMMONIUM BASES.

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In continuation of the researches on the indirect formation of double salts, it was thought desirable to test the further applicability of the indirect method used in the preparations of the double salts already described. It was found that this method was applicable not only to the formation of double salts which cannot be obtained by direct means, but also to the preparation of other salts which can be obtained by the direct method, *viz.*, the solution of the insoluble metallic component in the other soluble constituent and crystallization of the double salt from the solution. The preparation of double cupric iodides is not possible directly, since cupric iodide is not stable by itself and decomposes into cuprous iodide and iodine as soon as it is precipitated, or rather, liberated in chemical reactions. It is only when the indirect method is applied that the salt formation is successful. This, as has been pointed out before, is due to the fact that, when the cupric iodide is liberated in the presence of a large excess of ammonium iodide, it at once combines to form the double salt before it has time to decompose into its constituents. This behavior brings the conception of nascent molecules into prominence. The same reason applies to the formation of double carbonates of the alkaline earth metals and lead with potassium carbonate. These could not be prepared by the direct method, *viz.*, the solution of the carbonates of the alkaline earth metals and lead in potassium carbonate. For the preparation of these double salts, the indirect method was employed. This consisted in the precipitation of the carbonates of the alkaline earth metals and lead in the presence of a large excess of a strong solution of potassium carbonate; so that reaction took place between substances in the nascent state, and hence proceeded more readily. In addition to serving for the

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[1] Previous communications on the subject:

I. "The Double Platinic and Cupric Iodides of Substituted Ammonium Bases," Datta, *J. Chem. Soc.*, **103**, 426 (1913).

II. "Double Carbonates of the Alkaline Earth Metals and Lead with Potassium Carbonate," Datta and Mukherjea, *Proc. Chem. Soc.*, **29**, 185 (1913).

III. "The Double Cadmic and Mercuric Iodides of Substituted Ammonium Bases," Datta, THIS JOURNAL, **35**, 949 (1913).

IV. "Iodoplatinates of Substituted Ammonium and Sulfonium Bases," Datta, THIS JOURNAL, **35**, 1185 (1913).

preparation of double salts, not obtainable by direct means, the indirect method may also be used for the preparation of double salts which can also be prepared by the direct method. This applies to the preparation of double platinic iodides of the substituted ammonium bases which have been prepared by precipitating solutions of the ammonium iodides by chloroplatinic acid. The preparation of double mercuric iodides is a parallel case. Several double mercuric iodides were prepared by the direct method, *viz.*, solution of mercuric iodide in solutions of the alkylamine iodides and crystallization of the double iodide from the resulting solution. The indirect method, however, has done away with the preparation of mercuric iodide at the outset, a solution of mercuric salt added to an excess of substituted ammonium iodide serves for the production of the double salt. In cases of preparation of double salts of other types, however, where an excess of mercuric iodide solution has to be ensured, a solution of mercuric iodide in the potassium iodide has been conveniently used. Similarly, several double cadmium iodides have been prepared by the indirect method.

It is necessary to point out that indirect salt formation fails with the substituted ammonium bases with radicals of low molecular weight, owing to the extreme solubility of the double salts. Nevertheless, the method is susceptible of wide application, being applicable to the formation of double salts generally. The preparation of other double iodides of the series has been undertaken to test the further applicability of the method.

Experimental.

The Double Platinic Iodides (*Iodoplatinates*).—Several of the double platinic iodides of substituted ammonium and sulfonium bases have been described before.[1] It was thought possible that further study might reveal additional points of interest. As is evident, from the former researches, platinic iodide forms double salts of the type $2NR_4I.PtI_4$ only with the alkali metals and the ammonium and sulfonium bases. With, however, piperidinium and coniinium iodides, double salts of the type $4NR_4I.PtI_4$ have been prepared; with guanidinium iodide, a salt of the type $3NR_4I.PtI_4$ and with quinoline ethyliodide and quinaldine ethyliodide salts of the type NR_4I,PtI_4 have been obtained. Furthermore, several double iodides of the series are liquid, which is of considerable interest as affording examples of liquid double platinic iodides.

Piperidinium Platinic Iodide, $4C_5H_{11}NHI.PtI_4$.—On adding a solution of chloroplatinic acid to a strong solution of piperidine hydriodide, a black, shining, crystalline precipitate is formed. This is washed with a small quantity of water and dried in the desiccator. The salt is soluble in water to a beautiful red solution.

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[1] Datta, *J. Chem. Soc.*, 103, 426 (1913); THIS JOURNAL, 35, 1185 (1913).

0.2031 g. gave 0.0262 g. Pt; calc. for $4C_5H_{10}NH_2I.PtI_4$; Pt = 13.12; found, 12.91.

Coniinium Platinic Iodide, $4C_8H_{17}NHI.PtI_4$.—As piperidine forms a salt of the type $4NR_4I.PtI_4$ it was to be anticipated that coniine, which is α-propylpiperidine, would also form a salt of the same type. This has been found to be the case. The double iodide separates as a viscous, dark brown oil on adding chloroplatinic acid to a strong solution of coniinium iodide. This is repeatedly washed by decantation with water and dried as usual in the desiccator.

0.2115 gave 0.0233 Pt; calc. for $4C_8H_{17}NHI.PtI_4$; Pt = 11.23; found 11.03.

Isoquinolinium Platinic Iodide, $2C_9H_7NHI.PtI_4$.—Isoquinoline hydriodide, prepared by neutralizing isoquinoline with hydriodic acid, gave on evaporation a yellowish crystalline powder which on keeping in a desiccator turns reddish violet. The freshly prepared salt is dissolved in water and to it a 10% solution of chloroplatinic acid is added. A black precipitate is obtained which is very sparingly soluble in water, forming a faint yellow solution. It is filtered and, after being washed repeatedly with water, dried in the desiccator. The salt consists of a dark chocolate colored powder.

0.2513 gave 0.0407 Pt; calc. for $2C_9H_7NHI.PtI_4$; Pt = 16.02; found 16.21.

Guanidinium Platinic Iodide, $3CH_5N_3HI.PtI_4$.—Guanidine hydriodide is prepared by neutralizing guanidine carbonate with hydriodic acid and evaporating on the water bath. The double iodide is obtained as a fine, black crystalline precipitate, the solution at the same time turning intensely red. The salt is dried as usual and analyzed.

0.2815 gave 0.0438 Pt; calc. for $3CH_5N_3HI.PtI_4$; Pt = 15.43; found 15.53.

Quinoline Ethyl Platinic Iodide, $C_9H_6(C_2H_5)NHI.PtI_4$.—This is obtained as a greenish black precipitate by adding chloroplatinic acid to a solution of quinoline ethyliodide. The salt is very sparingly soluble in water. The filtrate from the precipitate is colored dull yellowish green.

0.2115 gave 0.0417 Pt; calc. for $C_{11}H_{11}NHI.PtI_4$; Pt = 19.95; found 19.72.

Quinaldine Ethyl Platinic Iodide, $C_{10}H_9N.C_2H_5I.PtI_4$.—Quinaldine ethyl iodide is only sparingly soluble in water. To a saturated solution of this salt, chloroplatinic acid is added. A momentary light brown precipitate is formed which changes at once to a dirty black-brown. The filtrate has a very faint green color with a faint red fluorescence, and after a day's staying it deposits a further quantity of the precipitate and turns colorless. The salt is highly insoluble in water.

0.3021 gave 0.0591 Pt; calc. for $C_{10}H_9N, C_2H_5I.PtI_4$; Pt = 19.46; found 19.61.

Methylethylpropylphenylammonium Platinic Iodide, $N(CH_3)(C_2H_5)(C_3H_7)(C_6H_5)I.PtI_4$.—This is obtained as a black-brown precipitate by the usual method. The salt is very sparingly soluble in water, the filtrate from the precipitated salt having a very faint green color with a red fluorescence.

The filtrate, on standing, like the preceding salt deposits a further quantity of the precipitate, the solution turning colorless.

0.2631 gave 0.0514 Pt; calc. for $C_{12}H_{20}NI.PtI_4$; Pt = 19.34; found 19.55.

The Double Cupric Iodides.

In addition to the double cupric iodides which have already been described,[1] the following have been prepared by precisely the same method: They are interesting on account of the fact that some of them represent new types and that some of them are liquid at the ordinary temperatures.

Tripropylammonium Cupric Iodide, $3N(C_3H_7)_3HI.2CuI_2$.—A saturated solution of cupric chloride is added to tripropylammonium iodide, when a dark brown oil is precipitated which sinks under water. This is not decomposed by water as was observed previously with some of the higher members. It is washed by stirring with repeated quantities of water in a basin and pouring off the wash water. Finally, the oil is allowed to dry in the desiccator. The compound consists of a dark brown viscous oil.

0.1798 gave 0.0184 CuO; calc. for $3N(C_3H_7)_3HI2.CuI_2$; Cu = 8.67; found 8.16.

Trimethyl-p-tolylammonium Cupric Iodide, $N(CH_3)_3C_7H_7I.CuI_2$.—To a saturated solution of trimethyl-*p*-tolylammonium iodide, a saturated solution of cupric chloride is added, when a brick-red precipitate falls down. This precipitate is unaltered by large quantities of water and hence could be washed freely. It is dried in the desiccator.

0.2631 gave 0.0337 CuO; calc. for $N(CH_3)_3C_7H_7I.CuI_2$; Cu = 10.60; found 10.23.

Isoquinolinium Cupric Iodide, $2C_9H_7NHI.CuI_2$.—When a saturated solution of cupric chloride is added to a saturated solution of isoquinoline hydriodide, a dark pasty substance is first precipitated which gradually solidifies on stirring with a glass rod. The solidified substance is finally broken up in a mortar and sucked to free it from the adhering mother liquor, when it is obtained as a brown crystalline powder.

0.4364 gave 0.0382 CuO; calc. for $2C_9H_7NHI.CuI_2$; Cu = 7.58; found 6.98.

Triethylsulfonium Cupric Iodide, $2S(C_2H_5)_3I.CuI_2$.—When a saturated solution of cupric chloride is added to a saturated solution of triethylsulfonium iodide, a red-brown oil is precipitated, which appears black in thick layers. The oil is not washed with water since it appears to be decomposed, giving a dirty brown emulsion.

0.2544 gave 0.0230 CuO; calc. for $2S(C_2H_5)_3I.CuI_2$; Cu = 7.78; found Cu 7.22.

Hence cupric iodide forms, altogether, three types of salt, *viz.*, $2NH_4I.CuI_2$, $3NR_4I.2CuI_2$ and $NR_4I.CuI_2$. Of these the first is generally produced and the second and third types are formed only in exceptional cases.

The Double Silver Iodides.

In continuation of the researches on the indirect formation of double salts, the preparation of double silver iodides was undertaken. It is

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[1] *Loc. cit.*

necessary to point out that by the direct method, *viz.*, the solution of silver iodide in solutions of the alkali, ammonia and pyridine hydriodides, corresponding double salts were obtained by other investigators. The only instance of a double silver iodide prepared by the indirect method is tetraethylammonium silver iodide, $N(C_2H_5)_4I.2AgI$ by Stromholm.[1] He prepared the salt by adding silver nitrate to a solution of tetraethylammonium iodide.

It is interesting to note that the formation of the double salts of silver by the indirect method only holds with the substituted ammonium bases of high molecular weight. With the low molecular weight substituted ammonium bases, the formation of double salts does not take place, pure silver iodide being the precipitate on the addition of silver nitrate to the ammonium iodide solutions. This is due to the small affinity between silver iodide and the alkali and ammonium iodides. It is for this reason that those double iodides of silver with the alkali metals and ammonia which can be prepared by the direct method, are at once decomposed into the constituents when treated with water. It is to be noted that two series of salts have been obtained; with tetramethylammonium iodide, as well as with pyridine or quinoline hydriodide, salts of the type $NR_4I.2AgI$ are formed; but with tetrapropylammonium iodide, a salt of the type $2N(C_3H_7)_4I.3AgI$ is formed.

The following double iodides have been prepared by adding a solution of silver nitrate to a saturated solution of the substituted ammonium iodides.

Tetramethylammonium Silver Iodide, $N(CH_3)_4I.2AgI$.—To a strong solution of tetramethylammonium iodide a strong solution of silver nitrate is added, with constant shaking and stirring. A white precipitate, with a faint yellow tinge is obtained. This is filtered and dried in the steam chamber.

0.2271 gave 0.1553 AgI; calc. for $N(CH_3)_4I.2AgI$; Ag = 32.19; found 31.44.

This and other salts of the series are decomposed by boiling with dilute nitric acid, leaving pure silver iodide.

Trimethyl-p-tolylammonium Silver Iodide, $N(CH_3)_3C_7H_7I.2AgI$.—This is obtained as a white precipitate by adding a solution of silver nitrate to a moderately strong solution of trimethyl-*p*-tolylammonium iodide. The precipitate is washed with water and dried in the steam chamber.

Pyridinium Silver Iodide, $C_5H_5NHI.2AgI$.—This is obtained as a white precipitate by the usual method described above. It is dried in the steam chamber.

0.3005 gave 0.2057 AgI; calc. for $C_5H_5NHI.2AgI$; Ag = 31.70; found 31.39.

Quinolinium Silver Iodide, $C_9H_7NHI.2AgI$.—This is obtained as a white precipitate which is washed, and dried in the steam chamber.

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[1] *Ber.*, 36, 142 (1903).

0.2931 gave 0.1849 AgI; calc. for $C_9H_7NHI.2AgI$, Ag = 29.51; found 28.99.

Tetrapropylammonium Silver Iodide, $2N(C_3H_7)_4I.3AgI$.—With tetrapropylammonium iodide, quite a distinct type of salt is obtained, *viz.*, $2NR_4I.3AgI$, whereas in the case of other salts, the type $NR_4I.2AgI$ is produced. The latter type is the one usually formed whereas the former type is only exceptional, being obtained mainly with the heavy bases. The salt is obtained as a white precipitate by adding a solution of silver nitrate to tetrapropylammonium iodide. The precipitate is washed and dried at 100°.

0.2533 gave 0.1324 AgI; calc. for $2N(C_3H_7)_4I.3AgI$; Ag = 24.32; found 24.02.

Investigations on similar lines are being continued.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF THE MECHANISM OF THE GRIGNARD REACTION.

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Introduction.

Ever since the time when Grignard pointed out that the reaction between magnesium and alkyl or aryl halides was much facilitated if the latter were dissolved in ether, various opinions have, from time to time, been promulgated concerning the role of the solvent in the reaction. Evidence appears to be at hand pointing to the conclusion that the ether forms one or more definite compounds with the magnesium alkyl (or aryl) halide. Thus, in the case of methyl iodide, Grignard observed that an addition product of the formula $(C_2H_5)_2O.MgCH_3I$ was left, after the excess of ether had been removed in a vacuum. Grignard at first held the view that this molecule of ether functioned as ether of crystallization. Further evidence regarding the existence of definite compounds of ether and magnesium alkyl halides has been furnished by Tschelinzeff,[1] who showed that the addition of ether to a benzene solution of magnesium alkyl halide caused the evolution of definite and equal amounts of heat for each of the first two molecular quantities of ether added. Such an addition product would thus correspond to Zelinsky's compound $2(C_2H_5)_2O.MgI_2$.

A definite idea regarding the distribution of valences in the ether addition products was first put forward by Baeyer and Villiger,[2] who, with the work of Collie and Tickle[3] in mind, believed that they had in this class of compounds further evidence to strengthen their belief in the existence of tetravalent oxygen. Three years previously Collie and

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[1] *Ber.*, **37**, 2084 (1904); *Ibid.*, **37**, 4534 (1904); *Ibid.*, **39**, 773 (1906).

[2] *Ibid.*, **35**, 1201 (1902).

[3] *J. Chem. Soc.*, **75**, 710 (1899).