II.—*On the Formation of Organo-metallic Radicles by Substitution.*

By George Bowdler Buckton, F.R.S.

Up to the present time, there appear to be four different methods known for procuring the organo-metallic radicles. These are,

1st. By bringing the reducing action of sunlight to bear upon the haloïd compounds of the alcohol-radicles, in presence of a metal. As an example, the decomposition of iodide of methyl in presence of mercury, may be quoted. It would appear that iodine is here first set free, which combines with mercury. The nascent methyl also combines with mercury to form mercuric methyl, and, finally, these bodies coalesce into iodide of mercuric methyl, according to the equation,

$$\mathrm{HgI_2} + \mathrm{HgMe_2} = 2\,(\mathrm{HgMeI}).^{*}$$

2nd. By the action of potassium and sodium alloys of certain metals, upon the haloïds of the alcohol-radicles. As an illustration, the formation of trimethylarsine may be given.

$$3\,(\mathrm{MeI}) + \mathrm{As}\left\{\begin{array}{l}\mathrm{Na}\\ \mathrm{Na}\\ \mathrm{Na}\end{array}\right. = \mathrm{As}\left\{\begin{array}{l}\mathrm{Me}\\ \mathrm{Me}\\ \mathrm{Me}\end{array}\right. + 3\,\mathrm{NaI}$$

There is also an analogous reaction, representing the formation of a sesqui-ethylated lead-radicle.

$$\begin{array}{l}\mathrm{Pb}\\ \mathrm{Pb}\end{array}\left\{\begin{array}{l}\mathrm{Na}\\ \mathrm{Na}\\ \mathrm{Na}\end{array}\right. + 3\ \mathrm{EtI} = \begin{array}{l}\mathrm{Pb}\\ \mathrm{Pb}\end{array}\left\{\begin{array}{l}\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\end{array}\right. + 3\,\mathrm{NaI}$$

3rd. Perhaps the most general method of isolating the organo-metalloïds, is by decomposing the ordinary haloïds of the metals by zinc-methyl, or zinc-ethyl; or by substituting for these haloïds, salts of the organo-metals.

Thus for the first mode :—

$$4\,(\mathrm{PbCl}) + 2\left\{\begin{array}{c}\mathrm{Zn\ Et}\\ \mathrm{Zn\ Et}\end{array}\right\} = \begin{array}{l}\mathrm{Pb}\\ \mathrm{Pb}\end{array}\left\{\begin{array}{l}\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\end{array}\right. + 4\,(\mathrm{ZnCl}) + 2\mathrm{Pb}$$

and for the second mode :—

$$2\,(\mathrm{SnEtI}) + \left\{\begin{array}{c}\mathrm{ZnEt}\\ \mathrm{ZnEt}\end{array}\right\} = \begin{array}{l}\mathrm{Sn}\\ \mathrm{Sn}\end{array}\left\{\begin{array}{l}\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\end{array}\right. + 2\,\mathrm{ZnI}$$

4th. This method is founded on the displacement of the metal contained in the organo-metalloïd by another metal, which is sup-

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* Equivalent of mercury = 200. Corrosive Sublimate $\mathrm{HgCl_2}$.

posed to be in a more electro-positive or electro-negative state than that removed. The few experiments I have now to describe, are more particularly connected with this method of operating, and were undertaken, partly with a view to studying the interchange of the true metals contained in various organo-metalloïds, when acted upon by simple metals, or their salts, and partly for testing the action of the metalloïds themselves upon salts of other organo-metallic radicles.

In this manner it was thought some knowledge might be gained, as to how far the conversion of one metalloïd into another might be predicted from our previous acquaintance with the relative electro-positive or negative conditions of the metals employed.

From the well-known reaction represented by the equation

$$3\left\{\begin{matrix}\mathrm{ZnEt}\\\mathrm{ZnEt}\end{matrix}\right. + 2\,\mathrm{Na} = 2\left\{\begin{matrix}\mathrm{ZnEt}\\\mathrm{ZnEt}\end{matrix}\right\} + \left.\begin{matrix}\mathrm{NaEt}\\\mathrm{NaEt}\end{matrix}\right\} + 2\,\mathrm{Zn}$$

It has been thought that the alcohol-radicles play, in these metalloïds, an electro-negative part towards the respective metals. The extrusion of the zinc in zinc-ethyl, therefore, would be due to its less positive character towards sodium. Many instances occur in which iodine, bromine, &c., may be removed by zinc, sodium, &c., from salts of the organo-metallic radicles, thus affecting their reduction; but the question here proposed for solution was the order of substitution of the metal contained in the radicle by another metal.

From this mode of preparing sodium-ethyl, Mr. Wanklyn surmises that sodium will remove methyl from cacodyl, and take its place, an arsenical alloy being simultaneously formed.

I am not aware that the experiment has been performed, but I have tried a somewhat analogous reaction, triethyl-stibine being employed instead of cacodyl.

Some bright cuttings of sodium were placed in a tube charged with coal-gas, and covered with a few grammes' weight of triethyl-stibine. As no change was observed after three days' contact at ordinary temperatures, the tube was exposed for ten minutes to 160° C. At first, a few bubbles of gas were disengaged from the sodium, and a small quantity of a black deposit was formed, after which all action ceased. A subsequent examination of the contents of the tube, led to the conclusion, that the sodium was unalloyed with antimony, and that triethyl-stibine is, at the above temperature, unattacked by the metal sodium.

If we group together those metals known to combine with the alcohol-radicles, in the following order, which may, in a general manner, be supposed to represent their relative electric positions,

Chlorous or negative elements.	Basylous or positive elements.
O	H
Cl	K Na
Te	Mg
As Sb	Al
Ti Si Bo	Cd Zn
Bi	Hg
Pb	Sn
(Methyl ?)	(Ethyl ?)

we might expect an extrusion of the ethyl from triethyl-stibine even at ordinary temperatures, since that phenomenon is very marked, if mercuric ethyl be employed in place of triethyl-stibine.

Action of Sodium on Mercuric Ethyl.

As this reaction has been elsewhere fully described, I will only here state, that mercury is liberated in the form of a voluminous grey sponge, whilst the sodium-ethyl which is formed, is united in a very unstable condition with mercuric ethyl. This compound is spontaneously inflammable. It explodes violently, and resolves itself into an amalgam of sodium, ethylene, and hydride of ethyl gases.

The formation of the substance appears to be analogous to that of sodium-ethyl, with the difference that mercury is extruded instead of zinc.

The primary action is represented by the equation—

$$3\left\{\begin{matrix}\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\\ \mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\end{matrix}\right.+2\mathrm{Na}=2\left\{\begin{matrix}\left.\begin{matrix}\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\\ \mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\end{matrix}\right)\begin{matrix}\mathrm{Na\ Et}\\ \\ \mathrm{Na\ Et}\end{matrix}\end{matrix}\right\}+2\mathrm{Hg}+\begin{matrix}C_4H_4\\ C_4H_5H\end{matrix}$$

If I rightly understand Mr. Wanklyn, he thinks ethyl, &c., should be displaced by mercury, copper, and platinum. The above experiment does not appear to support this idea, since if sodium displaces mercury from mercuric ethyl, it is improbable that mercury would displace sodium from sodium-ethyl.

Bright zinc is not amalgamated when placed in boiling mercuric ethyl. If, however, finely granulated zinc be distilled with iodide of mercuric methyl, appreciable quantities of mercuric methyl pass into the receiver. By far the greater portion of the radicle, however, is split up into gases.

Action of Cadmium on Mercuric Ethyl.

5·6 grammes of mercuric ethyl were digested for some hours with 3·6 grammes of fused chloride of cadmium. The liquid acquired a dark colour, and exhaled a pungent odour, but I failed to isolate any salt of cadmium-ethyl, or the radicle itself.

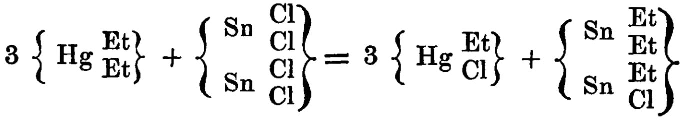
Zinc-ethyl acts powerfully on fused chloride of cadmium, and forms an unctuous mass, which fumes and finally inflames when exposed to the air.

The cadmium-ethyl remains combined with zinc-ethyl, and is almost entirely destroyed by distillation—a disadvantage also attending its formation from metallic cadmium and iodide of ethyl. This double compound, which seems to adhere to the chloride of zinc, cannot be broken up by solvents. I have attempted to do so with anhydrous ether, bisulphide of carbon, and benzol.

Metallic cadmium does not act on mercuric ethyl.

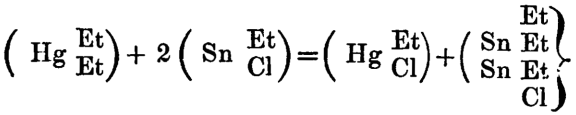
Action of Bichloride of Tin on Mercuric Ethyl.

These two substances react powerfully, and evolve at the same time great heat. A semifluid mass is formed, from which cold alcohol separates a highly pungent oil, which can be precipitated from the alcohol by water. This proved to be chloride of stannic sesqui-ethyl. The remaining mass of less soluble crystals had all the properties of chloride of mercuric ethyl. The change is represented by the equation—



$$3\left\{\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right\} + \left\{\begin{matrix}\mathrm{Sn}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\\ \mathrm{Sn}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\end{matrix}\right\} = 3\left\{\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right\} + \left\{\begin{matrix}\mathrm{Sn}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\\ \mathrm{Sn}\begin{matrix}\mathrm{Et}\\ \mathrm{Cl}\end{matrix}\end{matrix}\right\}$$

A similar result is obtained if we substitute chloride of stannethyl for bichloride of tin.



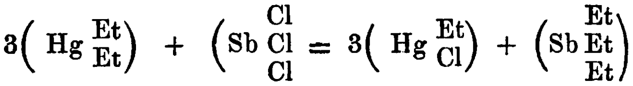
$$\left(\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right) + 2\left(\mathrm{Sn}\begin{matrix}\mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right) = \left(\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right) + \left(\begin{matrix}\mathrm{Sn}\\ \mathrm{Sn}\end{matrix}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right\}$$

Action of Terchloride of Antimony on Mercuric Methyl.

Very considerable heat is produced by the decomposition of these bodies, so much so, as to cause the reduction of a portion of mercury. About one part of terchloride of antimony appears to saturate three parts of mercuric methyl. The resulting mass of crystals, after repeated crystallization from alcohol, gave numbers agreeing with the formula of a double salt:—

$$3(\mathrm{HgMeCl}) + \mathrm{SbMe_3Cl_2}$$

The reaction with mercuric ethyl is slightly different. Part of the ethyl from the mercuric ethyl passes to the antimony to form triethyl-stibine, which becomes evident by its spontaneous inflammability. Boiling alcohol separates abundance of the crystalline chloride of mercuric ethyl, whilst a considerable quantity of antimony is thrown down by the energy of the action. This reduction is not, however, a necessary condition of the experiment:—



$$3\left(\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\end{matrix}\right) + \left(\mathrm{Sb}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right) = 3\left(\mathrm{Hg}\begin{matrix}\mathrm{Et}\\ \mathrm{Cl}\end{matrix}\right) + \left(\mathrm{Sb}\begin{matrix}\mathrm{Et}\\ \mathrm{Et}\\ \mathrm{Et}\end{matrix}\right)$$

It is believed that this and the foregoing experiments are, to a certain extent, in accordance with what we might theoretically expect from the relations of the metals to each other. Nevertheless, the reduction appears to be modified in extent, by the presence of the salt resulting from the reaction, and in no case is the reduction complete. We might have anticipated an entire separation of the ethyl from the mercury, perhaps with formation of bichloride of mercury.[*]

Action of Stannic Diethyl on Metallic Salts, &c.

Stannic diethyl may be boiled for hours with sodium at ordinary pressures, without undergoing change.

Stannic diethyl readily dissolves both iodide and chloride of mercuric ethyl, and again yields them unchanged by evaporation. If the chloride be strongly heated in a sealed tube, mercury is reduced and the pungent chloride of stannic sesquiethyl is formed, with ethylene and hydride of ethyl.

[*] It is remarkable that bichloride of triethyl-stibine is not attacked by zinc-ethyl, though the biniodide is readily decomposed.

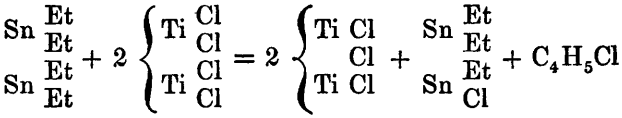
Action of Bichloride of Titanium on Stannic Diethyl.

Mr. Riley having kindly placed at my disposal some pounds weight of rutile, I prepared a quantity of bichloride of titanium, by passing chlorine at a low red heat over pellets made of a paste of powdered rutile, lamp-black, and a little gum.

The first crude product is often contaminated with sesquichloride of iron, but by distillation this may be readily removed, and what passes into the receiver is nearly pure.

Stannic diethyl mixes freely with the fuming bichloride of titanium, but no reaction commences until the liquids are heated, when there is an abundant evolution of gas. At the close of the experiment, a tenacious purple mass is obtained. On agitation with water, a heavy stratum separates from a fine purple aqueous solution, which last, when decanted and treated with dilute potash, precipitates a non-combustible purplish-violet body. This substance rapidly becomes white in the filter, absorbs oxygen, and is converted into titanic acid. The aqueous solution is therefore nothing but sesquichloride of titanium, described by Rose and others.

An examination of the lower stratum, which is terribly pungent, proved it to be chloride of stannic sesquiethyl. Taking the evolution of gas into consideration, the change is represented by the equation—



$$\begin{matrix}\mathrm{Sn}\begin{matrix}\mathrm{Et}\\\mathrm{Et}\end{matrix}\\ \mathrm{Sn}\begin{matrix}\mathrm{Et}\\\mathrm{Et}\end{matrix}\end{matrix} + 2\left\{\begin{matrix}\mathrm{Ti}\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\\ \mathrm{Ti}\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\end{matrix}\right. = 2\left\{\begin{matrix}\mathrm{Ti\ Cl}\\ \quad\mathrm{Cl}\\ \mathrm{Ti\ Cl}\end{matrix}\right. + \begin{matrix}\mathrm{Sn}\begin{matrix}\mathrm{Et}\\\mathrm{Et}\end{matrix}\\ \mathrm{Sn}\begin{matrix}\mathrm{Et}\\\mathrm{Cl}\end{matrix}\end{matrix} + C_4H_5Cl$$

My own experience coincides with that of M. Cahours, that salts of titanium do not furnish titanic ethyl when distilled with zinc-ethyl. The reaction is very violent, but difficulties interpose similar to those noticed in the preparation of cadmium-ethyl. There are good reasons for supposing, however, that, as soon as titanic ether has been prepared, titanic ethyl may be obtained from it, through the instrumentality of zinc ethyl.*

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* I have not been fortunate in obtaining titanic ether by distilling together titanate of potassium and sulphovinate of potassium. Chloride of titanium yields with sulphovinate of potassium, a distillate, boiling at 92°, composed of mixed alcohol, hydrochloric acid, and chloride of ethyl. Sulphates of titanium and potassium remain in the retort.

This reaction would be analogous to that lately made known by Dr. Frankland, in the preparation of boric ethide and boric methide;—a reaction very interesting, since it tends to show that oxygen as well as chlorine is, in certain instances, capable of substitution by ethyl.* I may mention, also, that plumbic acid, Pb_2O_4 powerfully acts on zinc ethyl with reduction of the lead. I have not taken the necessary steps, by this means, to isolate plumbic ethyl, but I think it highly probable that under reduced atmospheric pressure, the radical may be thus procured by distillation.

Titanium in its properties is, perhaps, more nearly allied to silicon than to tin, and considerable difficulty has been hitherto found in combining silicon with ethyl. It can scarcely be doubted that these bodies exist, and may hereafter show themselves through some well devised reaction.

A resinous mass is obtained by acting on mercuric ethyl with bichloride of titanium, and much chloride of mercuric ethyl is produced.

If we reason analogically from the tin reactions with mercuric ethyl, we should expect chloride of titanic sesquiethyl to be formed. I cannot yet confidently answer the question whether this body, or more simply the sesquichloride of titanium, is one of the products of the decomposition.

It is still a question of considerable interest how far, and in what manner, the introduction of different metals can be effected in organo-radicles represented by the type—

$$\begin{array}{c} R \\ \\ R \end{array} \left\{ \begin{array}{l} X+ \\ X+ \\ X+ \\ X+ \end{array} \right.$$

Can RR be represented by two different metals, in the same manner as X may represent different alcohol-radicles? It has been seen, that the result of the direct union of stannic diethyl with chloride of mercuric ethyl has not affirmatively answered the question as to the existence of chloride of mercuro-stannic sesquiethyl.

It is thought that the foregoing experiments, in their simpler forms, show that the metallic substitutions are pretty nearly those

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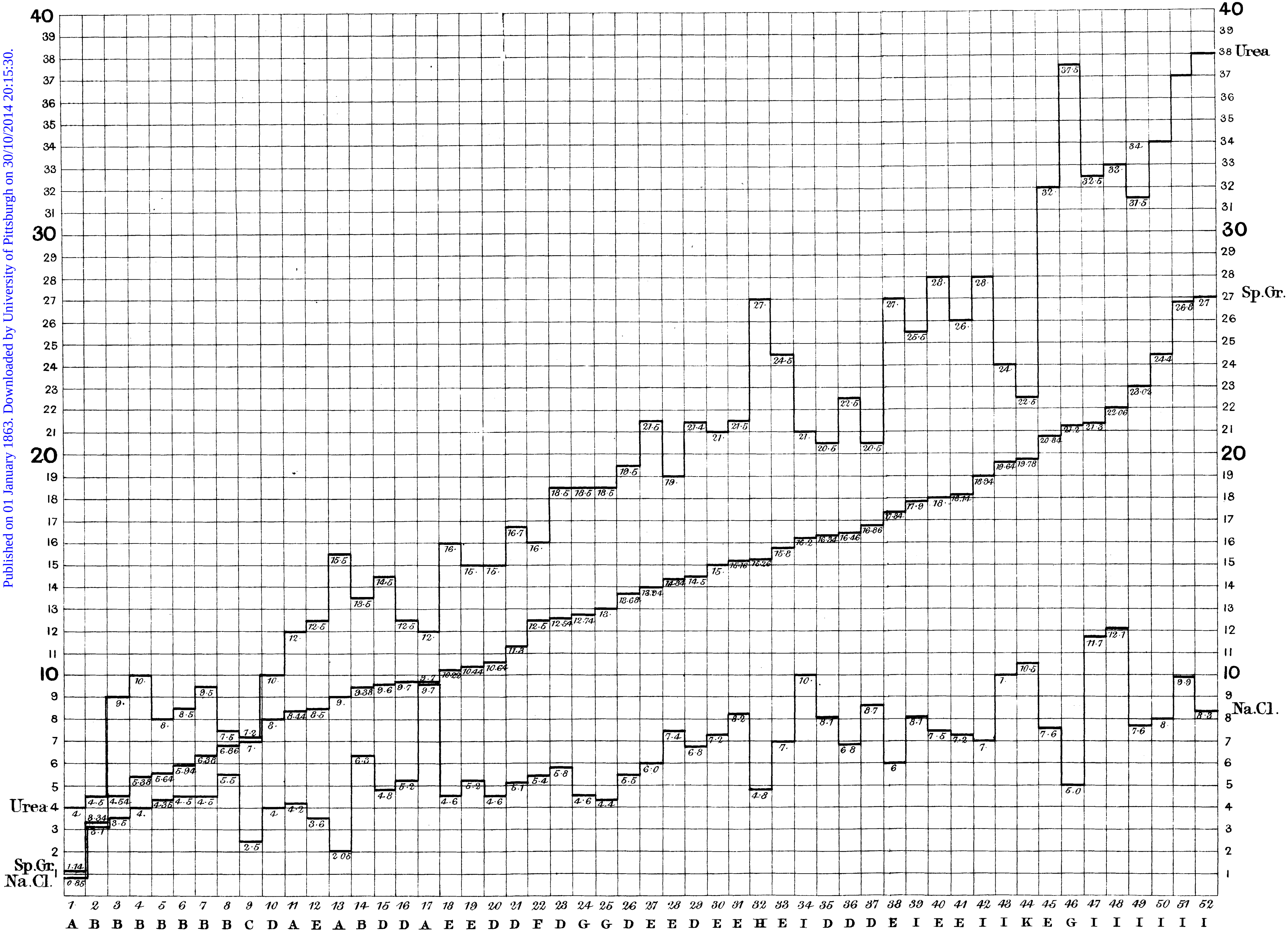
* M. Wurtz is inclined to think that, as ethyl has many analogies with chlorine, it may also take the place of peroxide of hydrogen; and he thinks this, in reality, happens in the formation of boric ethide.

52 ANALYSES OF URINE FROM 10 INDIVIDUALS.



indicated by their electro-position, but that the results are modified by the more or less saturated condition of the metals contained in the radicles.

Dr. Frankland observes, that the atomic powers of an organic radicle have reference to its stages of stability, dependent upon its points of saturation, and Dr. Hofmann expresses much the same, in stating that the basic properties of bodies intensify with the increase of their assimilated electro-positive alcohol-radicles.

The complete saturated condition of a body does not of necessity represent its most stable form. The sesquiethylated compounds of lead and tin are the most stable salts of those radicles, being capable, in some cases, of being distilled from aqueous caustic potash Triethyl-stibine is more stable that either tetrethyl- or pentethyl-stibine, and the same remark holds with respect to the ordinary chlorides of antimony.

It has been further shown, that the mercuric organo-metals may be partially, or entirely reduced by tin-compounds, and that stannic diethyl reduces bichloride of titanium to sesquichloride, ethyl being given up for chlorine.

I must express a hope that some of the missing numbers of this interesting and important group of substances will, through similar treatment, discover themselves to the chemist.