ART. XXI.—*On the Electrolysis of the Substituted Derivatives of Acetic Acid. Preliminary Notice;* by Dr. G. E. MOORE.*

MORE than a year ago the writer undertook, at the suggestion of Prof. Hermann Kolbe, the study of the phenomena attending the electrolysis of monocyanacetic acid. The question for whose solution the work was undertaken is the following:

It is well known that Kolbe obtained by the electrolysis of acetic acid a gaseous product, which he held to be identical with the univalent radical *methyl*. According to the generally received opinion the products of the action of chlorine, iodine, and bromine, etc., on acetic acid, stand in the very simple relation to the parent substance, that one or more atoms of hydrogen in the *methyl* group are replaced by a corresponding number of atoms of chlorine, iodine or bromine. According to analogy, therefore, the electrolysis of these substituted acids should result in the formation of substances which represent such substituted radicals. Prof. Kolbe formulated this reaction as follows:

$$2\left.\begin{matrix}H_2\\CN\end{matrix}\right\}C\left[\begin{matrix}C\\O\end{matrix}\right]OH+H_2O=2\left(\left.\begin{matrix}H_2\\CN\end{matrix}\right\}C\right)'+2CO_2+H_2O+H_2,$$

in other words, the univalent radical *monocyan methyl* $\left(\left.\begin{matrix}H_2\\CN\end{matrix}\right\}C\right)'$ was to be expected, a substance which would probably be either a gas or a readily volatile fluid.

For the purpose of answering this question, a quantity of rather more than 200 grm. of pure monocyanacetic acid was prepared, and purified from every trace of chlorine by a very tedious fractional crystallization of the lead salts of the mixture of monochlor- and monocyan-acetic acids first obtained.

With this material the electrolysis was performed in the month of December, 1870. The result obtained was decidedly *negative;* the expected substance could not be detected among the products of decomposition, and the question for whose solution the investigation was originally undertaken was therefore to be considered as settled.

It appeared desirable, nevertheless, to subject the products of the electrolysis to a more thorough examination. They are of very diverse nature, and their examination is by no means completed; as, however, temporary postponement of the work has become necessary, it may not be without interest to communicate a few of the more interesting results already obtained; all analytical data are reserved for a future detailed communication.

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If a concentrated neutral solution of pure potassium monocyanacetate, free from chlorine, be subjected to the action of the current from six Bunsen's elements, a voluminous evolution of gas ensues at the positive pole, which is, with the exception of a slight residue, soluble in potash solution. The unabsorbed portion appears to be, after the removal of a trace of gases absorbable by bromine, an entirely indifferent gas, probably nitrogen. The strongly acid solution in the positive cell, was, after the completion of the reaction, repeatedly shaken with ether and the latter distilled from the water-bath. The residue of the distillation, a deliquescent acid substance, was dissolved in a large volume of ether, the solution rendered neutral by agitation with the least possible quantity of potash solution, filtered and the ether distilled off from the water-bath. There remained a brownish residue, solid at ordinary temperatures, which agreed in its crystalline texture and other external properties, as well as in its fusing point (37°·8 C.), with ethylene cyanide $C_2H_4(CN)_2$. When boiled with a concentrated potash solution it evolves ammonia, and leaves a residue in which, by means of its suffocating vapor and reaction with ferric chloride, ethylene succinic acid may easily be detected.

The course of this phase of the decomposition may therefore be represented by the following equation:

$$2\begin{matrix}CH_2CN\\|\\CO\,.\,OH\end{matrix}+H_2O=\begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix}+2CO_2+H_2O+H_2,$$

precisely analogous to the reaction by which, during the electrolysis of potassium acetate *dimethyl* $\begin{matrix}CH_3\\|\\CH_3\end{matrix}$ is obtained.

The study of the associated products of the electrolysis being still incomplete, I abstain from a further development of the theoretical bearings of the facts already communicated until the missing data can be obtained.

As far as studied the reaction affords a very clear and positive evidence regarding the constitution of ethylene; it proves by a simple synthesis that this body is formed by the direct union of two methylene groups, and, that its formula should be written, in accordance with what is now the general usage $\begin{matrix}CH_2\\\|\\CH_2\end{matrix}$ and not, as it is still occasionally written, $\left(\begin{matrix}CH_3\\H\end{matrix}\right\}C\Big)''$, or, what is the same thing, $\left(\begin{matrix}CH_3\\|\\CH\end{matrix}\right)''$.

It is my intention to extend this investigation to the doubly and triply substituted acetic acids, and, as the corresponding

cyanogen derivatives are still unknown, I shall try if it be possible to obtain a similar series of reactions among the chlorine derivatives. Monochloracetic acid should give ethylene dichloride $\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix}$, and, by a precisely analogous reaction, we might expect from the electrolysis of dichloracetic acid acetylene tetrachloride $\begin{matrix}CHCl_2\\|\\CHCl_2\end{matrix}$. In the same manner the electrolysis of trichloracetic acid would probably yield dicarbon hexachloride $\begin{matrix}CCl_3\\|\\CCl_3\end{matrix}$.