XXXVII.—*On the Formation of Carbonic Ether.*

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WHEN oxalate of ethyl is heated with sodium or potassium, the metal dissolves, with evolution of a large quantity of carbonic oxide; and there is produced a dark-coloured mass, which, on distillation yields a liquid consisting, substantially, of carbonate of ethyl mixed with more or less undecomposed oxalate. This reaction, as is well known, was discovered many years ago by Ettling,* but has not yet found a satisfactory explanation based on experiment. In order to find out, if possible, the *rationale* of the process, we made a number of experiments, of which the following is a short account.

Starting with the assumption that the first step in the action of the potassium or sodium on oxalate of ethyl was the decomposition of some of the latter into carbonic oxide and potassium ethylate (EKO); we tried the action on oxalate of ethyl, of ready-formed sodium ethylate (ENaO), and soon found that this compound, like the metal itself, causes the formation of carbonic ether and carbonic oxide. If, for this purpose, ordinary so-called alcoholate (*i.e.*, the liquid obtained by dissolving sodium in perfectly anhydrous ethylic alcohol) be used, a considerable quantity of carbonic oxide is evolved; but the yield of carbonate of ethyl is very small, a great pro-

* *Annalen der Chemie und Pharmacie*, xix, 17.

portion of the oxalate, as well as of the temporarily formed carbonate, being changed into ordinary ether (E_2O), and sodium oxalate, and carbonate. A much better result is obtained, and the reaction goes on far more regularly, if the real compound $ENaO$ be used. Dry ethylate, $ENaO$, we easily succeeded in preparing, by evaporating the liquid alcoholate (prepared from alcohol previously dehydrated by distillation over sodium, in a current of dry hydrogen, within a retort heated in an oil bath) when the compound remained as a white porous mass, which, in an atmosphere of hydrogen, can be kept for a long time at 180° — 200° C without suffering apparent decomposition.* When dry ethylate of sodium is brought together with a large excess (eight times its weight, or more) of oxalic ether in the cold, it gradually dissolves, with slight evolution of heat and formation of a yellowish syrup, which sometimes gelatinizes on standing. Most probably a molecular compound of oxalate of ethyl and ethylate of sodium is produced, which, however, we did not succeed in obtaining in a definite shape. If this mixture is heated gradually—best by means of an oil-bath—a strong reaction is observed to set in at about 80° C.; large quantities of a gas (substantially carbonic oxide) are evolved, and the mass becomes darker and darker in colour—at last almost black. By gradually raising the temperature to about 140° the reaction is soon brought to a close. If the resulting mass is now distilled—we always carried out the distillation in a current of hydrogen, heating the retort in an oil-bath kept at temperature not exceeding 200° —there is obtained a *distillate* consisting of carbonate of ethyl mixed (or not, according to the relative proportions of materials used), with undecomposed oxalate, and invariably containing also a small quantity of ethylic alcohol, even if the most carefully dehydrated and dealcoholated substances were used.

* We are here bound to state, however, that in all our syntheses of $ENaO$, the weight of the compound, after complete desiccation at 180° C. (in dry hydrogen), was invariably short of that calculated from the weight of metal used, by from 3 to 6 per cent. of the calculated ethylate. In one of the experiments, for instance, in which alcohol freshly distilled off sodium, and perfectly bright sodium were used, 1.788 grms. of sodium gave 5.107 grms. of ethylate, i.e., 23 of Na gave 65.7 instead of 68 parts of $ENaO$. A titration of the substance with standard sulphuric acid led to the value 66.6. Some chemists say that alcohol cannot be completely dehydrated by means of sodium; if this be true, a part of the loss may have been owing to the formation of caustic soda.

The residue is black; it completely dissolves in water without evolution of a gas. The solution, on distillation, yields, substantially, pure water; more especially, no alcohol. The residue contains oxalate of sodium, a small quantity of formate, and besides these, the sodium salts of a complex of organic acids (Lowig's "nigric acid," *inter alia*), which we made many attempts to separate and define, but without success. There is not any carbonate produced; homologues of formic acid were specially searched for, but could not be detected. We never observed the formation of more than traces of ether; noteworthy quantities of the latter are formed only if the proportion of ethylate used is greater than the one above given; or if the mixture of ethylate and oxalate is rapidly heated before the ethylate is completely dissolved, by the local action of an excess of ethylate on the oxalate.

In order to obtain a basis for speculation on the nature of the reaction, we determined, in a series of experiments, made with varying proportions of carefully purified materials, the ratios to one another of the quantities of oxalate of ethyl and ethylate of sodium used, and of carbonic oxide, carbonate of ethyl, and alcohol produced. The purity of the oxalate was proved by titration. The ethylate, as a rule, was prepared *ex tempore* from a weighed quantity of sodium, and was dried in hydrogen at 180° – 200° , until it ceased to lose weight. In all these quantitative experiments, the quantity of oxalate used was at least 4 " $(\text{EO})_2\text{C}_2\text{O}_2$ " for 1 "E NaO ." The reactions were carried out, at the lowest possible temperature, in a distillation apparatus, the atmosphere of which communicated directly with that of a glass gasometer, continuously kept at a pressure equal to that of the atmosphere. The volume of gas evolved was determined by observing the expansion sustained by the atmosphere of the apparatus, and the observed volume, after applying the necessary corrections for temperature, pressure, and tension of water, reduced to weight. In one of these experiments, the gas was analyzed quantitatively, by passing a part of it (about four litres, four-fifths of the whole quantity); 1stly, through a U-tube containing pumice-stone and sulphuric acid, to absorb water, ether, and alcohol; 2ndly, through a weighed tube containing granulated soda-lime, and, at the exit end, chloride of calcium, to absorb carbonic acid; 3rdly, through a combustion tube filled with red-hot oxide of copper; and

4thly (the products of combustion), through a series of weighed absorption apparatus charged with sulphuric acid, potash, and soda-lime respectively, to absorb and determine the water and carbonic acid formed. Calculating the water formed for free hydrogen, the gas was found to contain in 100 parts by weight,

Hydrogen	0.1
Carbonic acid	0.4
Carbonic oxide	99.5

The ethereal distillate was weighed, and, at least qualitatively, tested for oxalate. In some cases, the proportion in it of carbonate of ethyl was determined by decomposing a weighed portion in a closed vessel with pure caustic soda, decomposing the carbonate of sodium formed with hydrochloric or sulphuric acid, and collecting the carbonic acid liberated (after previous absorption of water and alcohol by sulphuric acid), the bulk in solution of potash, the rest in granulated soda-lime. The quantity of oxalate of ethyl decomposable by a given weight of ethylate of sodium was found out by tentative experiments, *i.e.*, by adding to a weighed quantity of oxalate small successive quantities of ethylate, and, after each addition, heating as long as any more gas was evolved.

The successive volumes of carbonic oxide evolved (and probably also the quantities of carbonate of ethyl formed) were found to be proportional to the corresponding weights of ethylate of sodium added. Allowing the several experiments to mutually supplement each other, we were led to the following conclusions:—

“ ENaO ” parts of ethylate, acting upon an excess of oxalic ether, decompose 4“(EO) $_2$ C $_2$ O $_2$ ” parts of oxalate of ethyl, and produce 3“(EO) $_2$ CO” parts of carbonate of ethyl, 3“CO” parts of carbonic oxide, and about 0.4 “EHO” parts of alcohol. Each of the ratios here given is the result of a number of experiments, in which the direct experimental numbers came as near the integers here adopted as could be expected in experiments of this nature.

The experiments adduced up to this point were carried out in the University Laboratory, Edinburgh, during the winter session of 1867-68.* One of us has lately supplemented them (in

* At the Norwich meeting of the British Association (1868), the before-mentioned results were communicated, privately, to a number of chemists, among them to

Prof. Kekulé's Laboratory at Bonn) with a few experiments on potassium ethylate.

Dry ethylate of potassium is easily prepared in the same way as the sodium compound. The liquid alcoholate, when evaporated, in a current of dry hydrogen, in a retort heated by means of an oil-bath, leaves an oil, which, on continued exposure to 150° — 180° C., slowly gives up the last traces of alcohol, and leaves the compound EKO as a white mass. This body, in an atmosphere of dry hydrogen, stands a temperature of 200° without observable change. Its behaviour to oxalate of ethyl, qualitatively, is quite analogous to that of sodium ethylate, only the reaction is more energetic and commences at a lower temperature. But the quantity of oxalic ether decomposed, per atom of metal, was found to be far more considerable. A quantitative experiment gave the following numbers :—

1 $\times$ "EKO" (direct observation, $1.02 \times K + 0.98 \times EO$) in acting upon 12.9 " $(EO)_2C_2O_2$ " gave 6.7 "CO", and a distillate containing 6.2 " $(EO)_2CO$ ", 4.5 " $(EO)_2C_2O_2$ " and about 1.6 "EHO".

Taking all our results together, and considering especially that carbonic oxide and carbonate of ethyl were always produced in very nearly equal numbers of molecules, as if the greater part of the oxalate of ethyl had simply been split up into these two compounds, and that (in the case of potassium ethylate) the quantity of oxalate thus decomposed, per molecule of EKO used, amounted to upwards of six molecules, it is scarcely possible to evade the conclusion that, in the process considered, we have to deal with a catalytic reaction; *i.e.*, a cycle of reactions in which the ethylate is continuously decomposed and reproduced; and that a given weight of potassium ethylate could decompose unlimited quantities of oxalate of ethyl, if it were possible to exclude certain other reactions, which go on side by side of the main one, and gradually consume the ethylate. Whether or not these other reactions are an essential condition for the main reaction setting in at all, can, of course, be decided only by further experiments.

Professor Wanklyn said that in 1864 he had read a paper to the Society on "The Constitution of the Fatty Acids," wherein

Mr. Wanklyn. Compare the publications of that gentleman in *Chemical News*, 25th September, 1868; and *Phil. Mag.* (Memoir on Ethylate of Sodium).

he regarded the ethers as compounds in which the acid-forming radical is the metal, and the ethyl-oxide the chlorous radical. He also presented a paper on the reaction treated of by the authors, and predicted that ethylate of sodium would decompose oxalic ether, producing carbonic oxide and a carbonic ether, and that an unlimited quantity of oxalic ether might be decomposed by a given quantity of ethylate of sodium; but that paper was not published by the Society. It was gratifying to him to find his prediction verified so long afterwards by gentlemen who had made the experiment, without any communication with, and quite independently of, himself.