IV.—*Note on the Formation and on the Constitution of the Fulminates.*

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As the formula of the fulminates proposed by me is among those discussed by Dr. Divers in the foregoing communication, I may be allowed briefly to criticise his proposal and to state my present views on the subject.

The formula in question, $(\text{HO.N}) : \text{C} : \text{CH}(\text{NO})$ (which I should now prefer to write thus, $(\text{HO.N})\text{C.H.NO}$) was first publicly mentioned in the course of some remarks I made at a meeting of the Society on April 1st, 1875, when Professor Hofmann read a paper "On the Action of Ammonia and Sulphuretted Hydrogen on the Fulminates," the work of one of his students, Mr. R. Steiner.

My reasons for dissenting from Kekulé's formula are sufficiently stated in *Miller's Elements of Chemistry*, vol. iii, 5th edition, p. 176.

In proposing an alternative formula, I was led to assume that half the nitrogen was present in the form of nitrosyl, NO, and the other half in the form of *hydroximide*,* N.OH, because I took for granted that the fulminates were the products of the direct action of *nitrous acid* upon *alcohol*, it being known from Victor Meyer's researches that both of these groups could be introduced through the agency of nitrous acid; the assumption that the fulminates were nitroso-derivatives also appeared to account for the formation of *nitrotrichloromethane* on distilling them with bleaching powder, as it was known that certain nitroso-compounds were easily converted by oxidation into nitro-compounds.

But as Dr. Divers observes, Victor Meyer's more recent researches have shown that the radicle NO is not introducible into a CH₃ or CH₂ group by means of nitrous acid. My formula certainly requires modification on this account, the equation which I have given as expressing the primary reaction:

being thus far incompatible with our present state of knowledge as to the action of nitrous acid.

* Instead of terming N.OH derivatives *isonitroso*-compounds, it would have been far better had Victor Meyer chosen the appropriate and expressive name of *hydroximido*-compounds, and the terminal *hydroximide* instead of the inexpressive although shorter *oxim*.

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Dr. Divers, however, I think makes a somewhat similar mistake. Nitrous acid, and not its anhydride, must be the active agent, and therefore we may write his equation in the following manner, without affecting the formula which he deduces:

Here it is assumed that the CH_3 -group exchanges 2H for N.OH, a reaction which, so far as I am aware, is as entirely without precedent as that involving the exchange of H in CH_3 or CH_2 for NO under the influence of nitrous acid; the conversion of nitromethane into "methyl-nitrolic acid" might indeed be cited, but can scarcely be regarded as a parallel case.

Whatever may be the force of this objection, I am led to propound a different formula on what I consider to be far higher grounds, viz., from a consideration of what is probably the nature of the reaction between alcohol, nitric acid and mercury.

In the first place, it is not probable that the fulminate is the immediate product of the action of nitrous acid, however produced, upon alcohol. It is well known that when treated with dilute nitric acid, alcohol undergoes *hydroxylation*, being finally converted into "orth-oxalic acid," $\text{C}(\text{OH})_3.\text{C}(\text{OH})_3$, and Dr. Debus's classical research leaves little doubt that one by one the hydrogen-atoms are displaced by hydroxyl; in this way, the alcohol is converted first into "ethaldehydol" (comp. *Miller's Chemistry*, vol. iii, 5th ed., pp. 504, 715), and then probably into "hydroxyethaldehydol":—

This last-mentioned compound I am inclined to regard as the primary source of the fulminate, *which is formed from it by the simultaneous—or it may be consecutive—action of nitrous acid and hydroxylamine*:

* This formula is obviously not the only one which could be deduced, assuming the fulminate to be formed in the manner suggested.

That hydroxylamine may be formed by reduction of nitric or nitrous acid by ethaldehydrol, or more highly hydroxylised derivatives of alcohol, is in the highest degree probable, especially after Dr. Divers' recent communication on the production of hydroxylamine in the dissolution of metals by nitric acid.

The formula which I now propose differs but slightly from that previously brought forward, but it is a far better expression of our knowledge of the fulminates. The representation of the carbon-atoms as exercising "triad" instead of "diad"* functions certainly removes an obvious objection to my earlier formula.

Steiner's formula is inadmissible, both because, as Dr. Divers also remarks, it is a symmetrical expression, and because it is improbable that a *hydroximide* would furnish *nitrotrichloromethane*; this, however, it is proposed to test experimentally, and I shall also endeavour to prepare fulminates by operating in accordance with the hypothesis here put forward.

In the following paper "On Liebig's Production of Fulminating Silver without the Use of Nitric Acid," which has been received since this note was written, Dr. Divers and Mr. Kawakita show that even nascent nitrous acid, alcohol and a silver salt do not yield fulminate, and that nothing but an energetic oxidation of the alcohol by a mixture of nitric acid and either mercury or silver nitrate seems to be effective. This is entirely in accordance with the view which I here put forward.