KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 30th, 1899.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 September 1899 Dl. VIII).

The following papers were read:

Chemistry. — „*On the influence of water on the velocity of the formation of ether.*" By Prof. C. A. LOBRY DE BRUYN and Dr. A. STEGER.

(Read in the meeting of June 24th 1899).

In a previous communication [1]) we drew attention to the influence of water on the velocity with which oxyethyl or oxymethyl is sub-

[1]) Proceedings 1898 p. 166.

stituted for the nitrogroup in orthodinitrobenzene by sodium alcoholate. It appeared that the existence of constant coefficients of velocity was not at all, or very little affected by the presence of water in the methyl- or ethylalcohol, a fact which was explained by the circumstance that by far the greater part of the sodium is present as alcoholate in mixtures of water and alcohol containing even 50 % of water. The influence of the water present was however felt in the alteration of the numerical values of the constants due to the change of the medium; with ethylalcohol the change consisted of a diminution of the constants as the quantity of water present increased, with methylalcohol exactly the contrary took place.

The influence of water on the reaction under discussion could not be followed further than a 50 % mixture of water and alcohol, owing to the ever decreasing solubility of the dinitrobenzene. We pointed out therefore the desirability of finding a reaction, which would allow velocity determinations to be made, for both alcohols, from the absolute alcohol to pure water; the two different curves for the two alcohols must necessarily meet in the point corresponding to pure water, that is to the reaction with Na OH.

We have discovered such a reaction in the process of the formation of ethers from alkyliodides and alcoholates, in the special case in which methyliodide is employed; the solubility of this iodide in water being sufficient to permit of a determination of the velocity. With ethyliodide it was found that, owing to its smaller solubility, it was impossible to go further than 30% ethylalcohol (70% water) and 40 % methylalcohol (or 60 % water).

The reactions studied are thus:

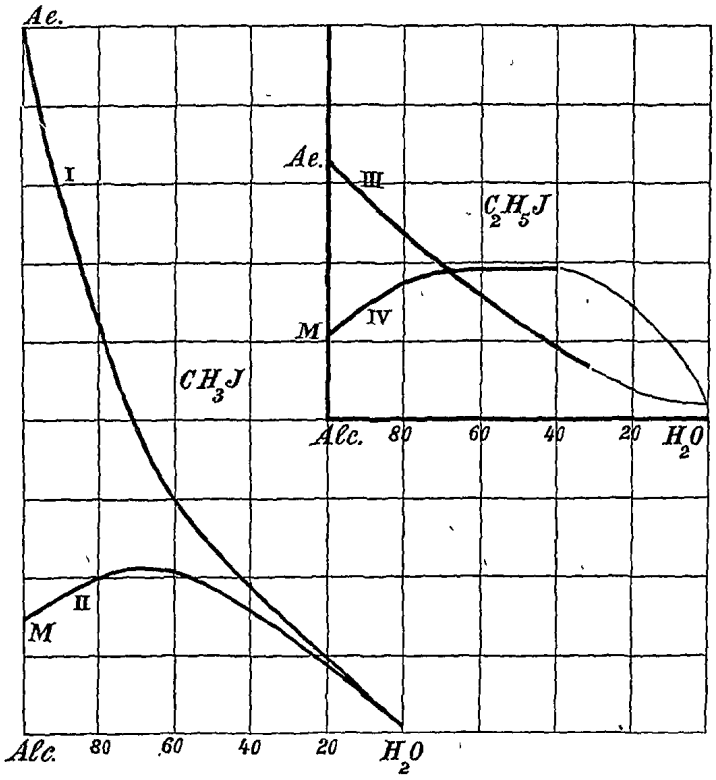
$$\text{I. } NaOC_2H_5 + CH_3I\,, \quad \text{II. } NaOCH_3 + CH_3I$$
$$\text{III. } NaOC_2H_5 + C_2H_5I\,, \quad \text{IV. } NaOCH_3 + C_2H_5I\,;$$

to which the change, $CH_3I + NaOH = CH_3ONa + NaI$, must be added.

The composition of the mixtures of water and alcohol was changed by equal steps of 10 % between absolute alcohol and water.

It was at once evident that the reaction-coefficients obtained in each experiment might be regarded as constants; with methylalcohol, the numbers are very satisfactory, less so with ethylalcohol, but still more than sufficiently so to show the change of velocity with the quantity of water present. For reaction I the numbers diminish from 0.189 for absolute alcohol to 0.0040 for water; for reaction

III, from 0,0168 to 0,005 ; for the reactions in methylalcohol (II and IV) an increase at first occurs with increasing content of water, for II there is a maximum at 70 % (0.032 to 0.0435) after which the numbers diminish to 0.004, for reaction IV the increase continues as far as the decomposition in 40 % alcohol (0.00525 to 0.0098) which was the extreme limit to which it was possible to go. The subjoined figure shows the change of the constants with the content of water.



It is thus evident that, as in the case of the reaction between o-dinitrobenzene and sodium alcoholate, the addition of water to ethylalcohol diminishes the velocity of the reaction, whilst with methylalcohol an increase first occurs which (reaction II) is followed by a decrease.

Attention may be drawn to some other conclusions. First, it appears that whilst for both iodides in methylalcohol there is a maximum for the mixture containing about 70 % of alcohol, the constants diminish regularly with methyliodide II, whilst with ethyliodide (IV) they remain practically constant between 40 % and 70 %. It is further seen that in the alcohol in which the electrolytic dissociation is the greater (methylalcohol) the velocity of

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reaction is the smaller, notwithstanding the fact that according to the researches of MENSCHUTKIN and CARRARA, methylalcohol itself accelerates similar reactions to a greater extent than ethylalcohol. It appears to us therefore that it follows from this case, as in the case of the reaction of o-dinitrobenzene and alcoholate, that reactions taking place in solvents other than water depend on circumstances which are as yet unknown, in addition to the degree of dissociation into ions.

From our earlier research we had concluded that the sodium dissolved in a 50 % mixture of alcohol and water is present mainly as alcoholate. The same conclusion may be drawn from an experiment in which a solution of 5 grams of Na in $^1/_2$ litre of a 50 % mixture of alcohol and water was warmed to 25° for 8 days with 32 grams (1 mol.) of ethyliodide. By means of several fractional distillations about 11.5 grams of ethylether were obtained, the theoretical quantity being 15.5 grams. Considering the unavoidable losses it may therefore be said that by far the greater part of the iodide was converted into ether.

It is still necessary to examine reactions such as those here studied, in mixtures of alcohol and water containing a large proportion of water, since in these there cannot be much alcoholate.

The details of this research will shortly be published in the "Recueil des travaux chimiques."

Chemistry. — Mr. Prof. H. W. BAKHUIS ROOZEBOOM speaks on: „*An example of the conversion of mixed crystals into a compound*".

(Read in the meeting of June 24th 1899.)

In the meeting of the 25th February 1897, page 376, I gave an explanation of the solidification of mixtures of optical isomers, when the solidification results in the formation (1) of a conglomerate (2) of mixed crystals, (3) of a racemic compound.

In a more complete paper, Zeitschr. phys. Chemie 28, 512, I have further developed the theory of the phenomena which must occur when these three types pass into each other when the solid mass is further cooled.

As one of the most interesting cases, Mr. ADRIANI, has at my request, studied an example of the conversion of mixed crystals into a compound below a certain temperature.

The example was camphoroxime. Mr. ADRIANI prepared the