Chemistry. — Dr. P. K. LULOFS: "*Substitution velocity in the case of aromatic halogen-nitroderivatives.*" (Communicated by Prof. LOBRY DE BRUYN).

(Read March 30, 1901).

Some two years ago Dr. ALPH. STEGER made an investigation of the velocity of the substitution of oxymethyl and oxyethyl for the nitro-group in ortho- and paradinitrobenzene [1]). This research included the influence exercised by a change of temperature, decrease of concentration, addition of a substance with a common ion and the regulated addition of water to the alcohol.

It now became important to extend this investigation to other substances. After preliminary experiments with various compounds, Dr. LULOFS has in the first place confined himself to chloro-, bromo- and iododinitrobenzene 1. 2. 4. Of these compounds it had been long since established that the halogen atom is liable to all kinds of substitution for instance by alkalis, ammonia, amines, alcoholates etc. It now appeared that the reaction with the last named substances lends itself very well to a quantitative research and for this reason sodium methoxide and sodium ethoxide were again chosen here.

As a first result it was established that the chlorine atom is much more easily replaced by oxymethyl or oxyethyl than the nitro-group in ortho- and paradinitrobenzene. It was further confirmed that of the three halogens the chlorine is the most and the iodine the least readily replaced by oxyalkyl; this had already been observed by KÖRNER by comparing the periods in which the reaction is ended. The constants for the reaction of the three halogen compounds with sodium ethoxide in absolute alcohol at the same concentrations are in the proportion of 3.26 : 2.03 : 0.455 (temp. 15°). It is remarkable that in the case of the aliphatic halogen compounds the behaviour of the halogens is just the reverse; in these compounds the iodine is in the weakest and the chlorine in the strongest combination with the carbon atom.

In the second place Dr. LULOFS studied the influence of the decrease of concentration on the constant. It had been proved by Dr. STEGER that the reaction between orthodinitrobenzene is not influenced by dilution. On the other hand CONRAD and BRÜCKNER [2]) had found that during the formation of an ether from an alkyl iodide and an alcoholate, this influence most decidedly exists in this sense that the reaction-constant increases with dilution.

[1]) Rep. Meeting 29 Oct. 1898; Dissertation 1898 and Recueil 18, 13.

[2]) Z. phys. Chem. 5. 289. This result was confirmed by STEGER (l. c.).

This last result, as we know, agrees with the electrolytic dissociation theory and may, therefore, be used in support of the view that the formation of ether is due to an ion-reaction. We are therefore confronted by the remarkable fact that the first reaction is not influenced by dilution whilst the second is affected by it, so that the second only should be considered as a reaction between ions.

In the reactions investigated by Dr. LULOFS, the reaction-constant is found to increase (as in the case of ether formation) with dilution and particularly when ethyl alcohol is used. In the case of chlorodinitrobenzene, the constant rises from 2.94 (gasconcentration) to 3.56 (one-fifth of that concentration); under the same circumstances the constant of the bromo-compound rises from 1.88 to 2.33.

It is a peculiar fact that the rise is much less marked when using sodium methoxide in methyl alkohol, being from 1.10 to 1.18 in the case of the chloro-compound.

In the third place, some experiments were made by Dr. LULOFS on the influence of the addition of a common (Na) ion. Dr. STEGER (l. c.) had found that this influence does not exist in the case of the reaction with orthodinitrobenzene, but that in the formation of ethers it is well marked, producing, in accordance with the electrolytic dissociation theory, a diminution of the reaction-constant. In the present case agreement with the last reaction was observed; for instance an addition of sodium bromide to the mixture of bromodinitrobenzene and sodium ethoxide caused a decided lowering of the constant.

We therefore see that in this case as well as in the case of dilution, the aromatic nitrohalogen compounds behave like the aliphatic halogen derivatives. The totally different behaviour of orthodinitrobenzene in an otherwise quite analogous reaction remains unexplained.

In the fourth place it was ascertained in what manner the reaction coefficients depended on the addition of water to the two alcohols. The reaction with orthodinitrobenzene and those in which ethers are formed had previously yielded very interesting results in this respect. [1]) Dr. LULOFS was in a position to show that chloro- and bromodinitrobenzene behaved in the same way. The coefficients remained constant even for an alcohol mixture containing 40 percent of water. In dilute ethylalcohol they decrease with the increase of the amount of water; on the other hand when dilute methyl alcohol is used they

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[1]) LOBRY DE BRUYN and A. STEGER. Proc. 30 Sept. 1899. Recueil 18, 41, 311.

first increase, then remain constant and finally decrease when the amount of water reaches about 40 percent. When using alcohol-water mixtures as solvent, it appeared that the decrease in concentration causes a rise and the addition of a substance with a common ion a lowering of the constant.

Dr. LULOFS research [1]), which may be usefully extended in various directions, points, like the results quoted, to the desirability of a study of the conductivity of the alcoholates when dissolved in the pure alcohols (partly carried out by CARRARA) or in mixtures of alcohol and water. It will then be possible to ascertain whether there exists a parallellism between the change of the reaction-constants and that of the conductivity.

Chemistry. — Professor BAKHUIS ROOZEBOOM presents a communication from Dr. A. SMITS: *„On the progressive change of the factor i as function of the concentration."*

(Read March 30, 1901).

Of the salts, which I have already investigated, KNO_3 [2]) is the only one for which the factor *i* decreases with increasing concentration. It, therefore, seemed to me very interesting to ascertain whether other nitrates behave similarly.

KNO_3 being an anhydrous salt, I purposely chose nitrates of which no hydrates are known.

In this investigation I have availed myself of my improved Landsberger apparatus [3]), which is sufficiently accurate for my purpose.

Before proceeding to mention the results, I will first draw attention to some points to which attention should be paid in the determination of boiling points by this method.

In determining the boiling point of pure water, it is noticed that the boiling point continuously rises during the progress of the experiment. In my apparatus this rise amounted 0.01^0 in 25 minutes. The explanation of this phenomenon is found in the continual increase in height of the column of water in consequence of the condensation of the aqueous vapour, which takes place. When the column of water increases in height, the pressure and consequently

[1]) Further particulars in his dissertation, Amsterdam, 1901.
[2]) Proc. 21 April 1900 714.
[3]) Proc. 26 May 1900 31.