78. *Reduction Potential of Isovaleraldehyde.*

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Applicability of dropping cathode for the research on reduction potentials (R.P.) of organic compounds has been proved by one of the present authors by the measurement of R.P. of nitrobenzene.¹⁾

The facilities of applying mercury dropping cathode, as it has been already proved, consist in the simplicity of its manipulation and the possibility of measuring minute quantities of reducible substance, for example, in case of nitrobenzene the R.P. is determinable in a solution so dilute as to contain 10^{-5} mol of it.

In the present work the R.P. of isovaleraldehyde has been determined in relation to the concentration of hydroion and the reduction product, i.e. isoamylalcohol, has been studied.

The measurements have been carried out with the mercury dropping cathode and "Polarograph."²⁾ The Polarograph is a photographic autoregistering apparatus, for tracing electrolysis current-voltage curves and has been very much used in the study of deposition potentials of metallic ions to mercury dropping cathode.³⁾

If the reduction of isovaleraldehyde should proceed in equilibrium at the mercury dropping cathode, the R.P. of isovaleraldehyde solution should be given by the following formula :

$$\pi = -\frac{RT}{2F} \ln \frac{K'' C_{R.CH_2OH}}{[H]^2 C_{R.CH_2O}} \quad (1)$$

in which $C_{R.CH_2O}$ denotes the concentration of isovaleraldehyde and $C_{R.CH_2OH}$ that of isoamylalcohol. It has been previously proved that the reduction of nitrobenzene at the mercury cathode proceeds in the equilibrium state.

Moreover, if we determine the reduction potential of isovaleral-

1) M. SHIKATA: Trans. Faraday Soc. No. 61 Vol. XXI p. 42-62 (1925).

2) T. HEYROVSKY and M. SHIKATA: Rec. Trav. Chim. des Pays-Bas Tome XLIV p. 496-498.

3) See for example, Rec. Trav. Chim. des Pays-Bas Tome XLIV p. 499-607.

dehyde, by taking the same current increment 1.9×10^{-8} amp. per 10 mv. in our measurement, $C_{R.CH_2OH}$ i.e. the concentration of reduced product is constant at the R.P.

So that we obtain for 20°C

$$\pi = - \frac{0.05812}{2} \log \frac{K'}{[H]^2 C_{R.CH_2OH}} \quad (2)$$

If we take the R.P. (i.e. at the point of current increment of 1.9×10^{-8} amp.) of 0.1N HCl solution, containing 0.1868 gr. mol per liter as standard (R.P. = -1.098 Volt) we can calculate the value of k'

$$\log k' = 34.6724.$$

In an acidic and an alkaline solution the formula (2) holds good to a satisfactory degree, only in a neutral solution R.P. being much positive than expected from the formula (2), that is to say isovaleraldehyde is reduced much easier in neutral solution than expected from the formula.

If we compare the R.P. of same hydroion concentration with various contents of isovaleraldehyde, we can obtain from the shifts of R.P., the coefficient of adsorption isotherm, by the formula proposed by one of us :

$$\pi = - \frac{RT}{2F} l_n \frac{K'''}{C_{R.CH_2OH}^m} \quad (3)$$

For an acid solution $m = 1.38$, and for an alkaline solution $m = 1.33$, revealing some positive adsorption of isovaleraldehyde to dropping mercury cathode. In a slightly acidic solution as well as in a neutral solution m is smaller than 1. For example in 0.1N NH_4Cl $m = 0.272$, and in 0.1N KCl $m = 0.287$.

It seems to be rather peculiar that m happens to be smaller than 1, for such examples have rarely been met with until now. That m is smaller than 1 means passivity of hydroion discharge or desorption of isovaleraldehyde from mercury surface. This is quite probable if we remind that nitrobenzene is in ordinary condition highly adsorbed by mercury surface, and only when mercury drop is under the influence of negative E.M.F., i.e. when the drop is negatively polarised, the negative charge arising from the negative polarisation expels nitrobenzene from the mercury surface, namely, the desorption of nitrobenzene occurs. If such desorption should occur in the case of isovaleraldehyde, we can expect that isovaleraldehyde would not be much influenced by the salting out action of a concentrated neutral solution.

In this respect nitrobenzene is much influenced by the salting out

action of neutral salt, which is seen by its acquiring much positive reduction potential.

Contrary to nitrobenzene, the isovaleraldehyde solution shows no conspicuous change of R.P. in a highly concentrated neutral solution, showing desorption must have taken place in this case. Although this is not the only explanation for the small value of m , the present authors are much inclined to take this view.

The height of saturation curve could be applied for the quantitative measurement of isovaleraldehyde. By this means the solubility of isovaleraldehyde in an aqueous solution is estimated to be 0.4475 gr. mol per liter. Further, by this method three reducible substances have been traced in isoamylalcohol of Kahlbaum's preparation. The most probable impurities of isoamylalcohol are aliphatic aldehydes, furfural and pyridine; the reduction potentials of furfural, pyridine, isovaleraldehyde, and isobutylaldehyde have been measured in a neutral as well as in a 0.1N NH_4Cl solution.

	Concentration	Solution	Reduction-potential			
			I.	II.	III.	IV.
Isoamylalcohol. (Kahlbaum)	3%	0.1N NH_4Cl	-0.880	-1.243	-1.599	—
Commercial iso- amylalcohol. (made in Japan)	0.1%	0.1N KCl	-1.060	-1.263	-1.438	—
„ (distilled)	1%	0.1N NH_4Cl	-0.888	?	-1.559	—
Isovaleraldehyde	$1.868 \cdot 10^{-3}m$	„	—	—	-1.553	—
Furfural	0.002%	„	—	-1.239	—	—
Isobutylaldehyde	1%	„	-1.056	—	—	—
Pyridine	$0.1251m$	0.1N KCl	—	—	—	-1.673

It will be seen that R.P. of second and third reducible impurities coincide with those of furfural and isovaleraldehyde, hence these two substances are most probably present in the isoamylalcohol tested.

As regard to Schiff's reagent for the aldehyde test, the limit of detectable concentration for isovaleraldehyde, is $1.868 \cdot 10^{-3}$ whereas by dropping mercury cathode it is $9.34 \cdot 10^{-5}$ i.e. the latter method exceeds the Schiff's test twenty times in sensitiveness.

Lastly, to give a decisive proof that the reduction product is isoamylalcohol, the influence of isoamylalcohol has been studied and found to follow the formula (1) in the first approximation.