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Chemistry. — "Action of hydrogen peroxyde on diketones 1,2 and on a-ketonic acids. By Prof. A. F. Holleman.

Some aromatic acids may be obtained by first introducing the acetyl group by means of the reaction of Friedel and Crafts and oxidising this to the carboxyl group. In many cases, however, this oxidation does not take place readily; the group CO.CH, yields with comparative ease the group CO.CO₂H but the further transformation of the latter into the carboxyl group is often attended with great loss. Even the method of Hoogewerff and van Dorf, consisting in heating the α -ketonic acid with concentrated sulphuric acid does not yield the theoretical quantity. I have tried whether this transformation might perhaps be attained quantitatively by means of hydrogen peroxide, according to the equation:

$$\frac{\text{R.CO. CO}_{2}\text{H}}{+ \text{ HO OH}} = \frac{\text{R.COOH.}}{+ \text{ HO CO}_{2} \text{ H (= H_{2}O + CO}_{2})}$$

This was indeed the case. Aqueous solutions of pyruvic acid, benzoylformic acid, thienylglyoxylic acid when heated with the calculated amount of 30 $^{\rm o}/_{\rm o}$ hydrogen peroxyde (Merck) at once eliminated CO and yielded almost quantitative amounts of acetic acid, benzoic acid and thiophenic acid. From Prof. Eykman, I received small specimens of four $\alpha\text{-ketonic}$ acids which he is investigating and these, when heated in aqueous or acetic acid solution with a slight excess of H_2 O_2 also eliminated CO. On titrating the acids obtained from them it was found that their group CO \cdot CO $_2$ H had passed into CO $_2$ H.

This result led us to suppose that α -diketones might also be readily resolved by the action of H_2 O_2 ,

$$\frac{\text{R.CO. CO.R}^1}{+\text{HO OH}} = \text{R. CO}_2 \text{ H} + \text{R}^1 \cdot \text{CO}_2 \text{ H},$$

Some of the diketones, such as benzil, camphorquinone and phenanthrenequinone were dissolved in glacial acetic acid and warmed for some days with a small excess of 30 %, H2 O2. The expected reaction took place almost quantitatively: it was remarkable that camphorquinone did not at once yield camphoric acid but first the anhydride, which was converted by boiling with dilute alkali into camphoric acid.

Messrs. J. Huisinga and J. W. Beekman have carried out the experiments.

Groningen, March 1904.

Lab. Univers.