exhausted, although sufficiently so to give only the green fluorescence of glass when connected to an induction coil, emits close to the oscillator a bluish glow, containing the characteristic bands of carbon impurities and hydroxyl.

For the moment, I have given up the use of these 1·90 m. waves and have built a 5-10 metre wave-length oscillator (about 80 watts), in order to see how the growing pressure of the mercury vapour modifies the spectra obtained. I use either the electrodeless discharge or a discharge with only one electrode (in a different apparatus). In the latter case, in a suitable apparatus, permanently evacuated and provided with a liquid air trap, this projects a glow the length of which may attain 40 cm. The pressure of the mercury vapour is varied by heating the mercury, and the degree of excitation by varying the distance between the electrode and the oscillator. I obtain in this way spectra which depend on the pressure and degree of excitation, and the one-electrode discharge does not give results quite identical with those of the electrodeless discharge. At 80°-90°, for example, the former does not clearly reveal the unclassified lines which Mr. Clarke mentions, except perhaps the line 2540. This fact is peculiarly striking for the line 3984·1; this line shows itself very feebly even in long exposures, though it is strong in the ordinary arc. The unclassified lines are found, however, in the electrodeless discharge. In the one-electrode discharge, the glow is observable in the region where the mercury condenses: it is violet; I was unable to discern any impurity, but found that the red lines 6234·35, 6123·46, and 6072·64 were strong in this light. The spectrum of the whole of the glow, taken longitudinally, shows a strengthening of the series $1P - mD$ and $1P - mS$; this is a pressure, and not a wave-length effect. At a higher temperature (110°-120°) and feeble excitation, I get a green glow which shows the Lord Rayleigh and Volkringer spectra (*Proc. Roy. Soc.*, A, 114; 1927. *Comptes rendus*, 1927, *passim*). I am continuing the study of the development of these spectra at increasing pressure, but, at the above-mentioned temperature, I find in this glow the yellow line 5790·6 ($1P - 2D$), and the violet line 4347 ($1P - 3D$), which does not agree with Mr. Clarke's observations: he only saw the triplets *s* and *d*. Mr. Clarke, however, does not say what was the pressure of mercury vapour in his experiment.

Briefly, the method described by Mr. Clarke is the well-known one of the separation of spectra by the electrodeless discharge. I am trying to see if this and the one-electrode method, used with very short wave-lengths (1·90 metres and 5-10 metres), give new results. Up to now, I have not noticed any modification in the emitted wave-lengths, which was to be expected, and the relative alterations in the intensity of the lines are effects of pressure or strength of excitation, and not to be attributed to the shortness of the wave-length used.

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The Formation of Citric Acid by *Aspergillus niger*.

IN two recent publications (*Jour. Chem. Soc.*, 200, 3044; 1927) we have presented results which are in agreement with the assumption that the conversion of glucose to citric acid by *Aspergillus niger* proceeds according to the scheme: glucose → gluconic acid → saccharic acid → citric acid.

It was suggested by Franzen and Schmitt (*Berichte der Deutschen Chem. Ges.*, **58**, 222; 1925) that the precursor of the citric acid of plants is β-γ-diketoadipic acid, arising from saccharic acid by loss of water. They showed that the ester of the diketo-acid is easily converted to citric acid by alkali hydroxide, a transformation of the benzilic acid type:

$$\mathrm{COOH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHOH \cdot COOH} \longrightarrow \quad -2\mathrm{H_2O}$$

$$\mathrm{COOH \cdot CH_2 \cdot CO \cdot CO \cdot CH_2 \cdot COOH} \longrightarrow \quad +\mathrm{H_2O}$$

$$\mathrm{COOH \cdot CH_2 \cdot \overset{OH}{\overset{|}{C}} \cdot CH_2 \cdot COOH}$$

$$\mathrm{\overset{COOH}{\overset{|}{}}}$$

This observation strongly supports their view, but apart from the recognition of diacetyl $\mathrm{CH_3 \cdot CO \cdot CO \cdot CH_3}$ (a decarboxylation product of diketoadipic acid) in ethereal oils, no further evidence has been adduced in favour of the participation of the diketo-acid in citric acid synthesis either by higher plants or by moulds.

Owing to the instability of diketoadipic acid, experiments on its behaviour to *A. niger* are not yet completed. Meanwhile, it appeared probable that useful indications on this point could be obtained by studying the growth of the mould on adipic acid. One of us (T. K. W.) has shown that *A. niger* readily oxidises certain fatty acids in the β-position, and therefore might be expected to convert adipic acid to the β-γ-diketo-derivative:

$$\mathrm{COOH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH} \longrightarrow$$
$$\mathrm{COOH \cdot CH_2 \cdot CO \cdot CO \cdot CH_2 \cdot COOH.}$$

If the mould is capable of effecting a 'benzilic-transformation' the production of citric acid might then be expected. This has now been demonstrated. Potassium citrate has been isolated from cultures of *A. niger* on the potassium hydrogen salt of adipic acid, and on potassium muconate,

$$\mathrm{COOK \cdot CH : CH \cdot CH : CH \cdot COOK,}$$

and characterised as the tri-*p*-nitrobenzyl ester in each case. In the adipic acid experiment thallous citrate was also prepared and analysed. The muconic acid may give rise to citric acid by addition of two molecules of water forming β-γ-dihydroxyadipic acid,

$$\mathrm{COOH \cdot CH_2 \cdot CHOH \cdot CHOH \cdot CH_2 \cdot COOH,}$$

which on oxidation could yield the diketo-acid and finally citric acid. The conversion of fumaric and crotonic acids in the presence of liver tissue to malic and β-hydroxybutyric acids (Dakin, "Oxidations and Reductions in the Animal Body," pp. 49-50) indicates the biological possibility of this suggestion.

The conceivable formation of citric acid from muconic acid by addition of four hydroxyl groups and formation of saccharic acid receives less support from the biological side. Further work is in progress which, it is hoped, may enable the mechanism of citric acid formation from carbohydrates and organic acids to be definitely elucidated.

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Extension of the Irregular Doublet Law.

RECENT work in this laboratory has shown that the irregular doublet law, first discovered in 1920 by G. Hertz in the X-ray region, and since then extended by Millikan and Bowen for the optical region, is capable of much wider application. Millikan and Bowen have applied the law for the prediction and identification of spectra of atoms which are stripped

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