THE ACTION OF LIGHT ON CATALYTIC OXIDATION BY SOME METALLIC COMPLEX SALTS.

(Preliminary Note)

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Received June 3rd, 1931. Published August 28th, 1931.

Since some ten years, Yuji Shibata, Keita Shibata and their collaborators have published a series of papers on the investigations of an enzyme-like oxidising action shown by some metallic complex salts.(1) · In studying this interesting reaction from various sides, especially from the investigations of its chemical kinetics, they came to a conclusion that the oxidation just mentioned must be produced by activated water-molecules and the role of complex salt added appears to be of rendering water-molecules catalytically active.

The present experiment has been carried out to study the influence of light energies on this catalytic oxidation, for the purpose of ascertaining what region of light spectrum will be effective to promote this reaction, that is to say, is it either the light which is absorbed by the complex salt used as oxidiser, or the light of longer wave-lengths which is absorbed by water-molecules? In this preliminary work, we used, as colour filters, plates of ordinary window glass (opaque for the ultra-violet light of wave-lengths shorter than $\lambda = 3300\,\mathring{A}$), ruby glass (transparent for light of wave lengths longer than $\lambda = 5900\,\mathring{A}$), green glass (transparent between $\lambda = 5860\,\mathring{A} - 3250\,\mathring{A}$), and finally 20% copper sulphate solution of 12 m.m. layer.

The reaction bulb of Warburg's apparatus which was used in our recent investigation of asymmetric oxidation(2) was illuminated by a Mazda-lamp of 100 W., in putting the colour filter between the light source and the reaction bulb. In this way, *d*-catechin was oxidised by racemic [Co en_2NH_3Cl] Br_2 and the pressure-depression (namely oxygen obsorption) in the apparatus was recorded time after time; the curves thus obtained are given in Fig. 2. As will easily be seen in these curves, the reaction velocity under green light is distinctly inferiour to those under red and white lights.

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(1) Y. Shibata und K. Shibata: Untersuchungen über die oxydasenartigen Wirkungen gewisser Metallkomplexsalze; *Acta Phytochimica*, **4** (1929), 363. Compare also Y. Shibata and R. Tsuchida; Studies on Asymmetric Oxidation; This Bulletin, **4** (1929), 142 and **6** (1931), 210. The references of papers on this subject which have been published in the Japanese language on the Journal of the Chemical Society of the Japan since 1920 are fully given in the papers just mentioned.

(2) Y. Shibata and S. Goda: Studies on asymmetric Oxidation. Part II., loc. cit.

On the other hand, we have observed the absorption spectrum of the solution of diethylenediamine-monoammonio-monochloro-cobaltic bromide and confirmed that the solution shows two absorption bands at $\lambda = 5000$ Å and $\lambda = 3640$ Å⁽¹⁾, both of which are just contained in the spectrum region transmitted by the green filter, while the red filter entirely absorbs that part of spectrum, where stand these two bands. From these results it may surely be insisted that excited molecules of water (under red and white lights) are more effective than equally excited molecules of the complex salt (under green light) for promotion of oxidation of *d*-catechin*. Then we carried out another experiment in making use of 20% $CuSO_4$-solution (liquid layer =12 m.m.) as the filter, because it is well known that this solution absorbs almost completely the infra-red and red part of spectrum, transmitting all other rays of shorter wave-lengths than yellow.

The pressure-time curve obtained under the $CuSO_4$-filter coincides very well with that under the green filter, or, in the other words, the light which lacks the infra-red and red parts in its spectrum is always less effective for promotion of this reaction than the light containing the infra-red and red rays.** Thus we are now convinced that our earlier explanation on this oxidation reaction was quite correct: namely it deals with the action of activated water-molecules and the reaction may perhaps be represented by the following scheme:

$$R + 2\,H \cdot OH + \frac{1}{2}O_2 = R(OH)_2 + H_2O$$

or further

$$R(OH)_2 = RO + H_2O$$

The ordinary associated molecules of water will be activated (very probably dissociated into monomolecular state) in coming to contact with some metallic complex salts which are endowed with this nature. Only the mechanism of this latter action is not yet quite clear.

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(1) Compare Y. Shibata: Recherches sur les spectres d'absorption des ammine-complexes metalliqes, I, *Jonrn. Coll. Scien. Imp. Univ., Tokio,* **37** (1915), Art. 2.

* The absorption spectrum of catechin has been studied by T. Tasaki *Acta Phytochimica,* **3** (1927), and it was found that the dilute solution of this substance shows an absorption band at $\lambda = 2780$ Å. Therefore, in the present case, where an ordinary electric lamp is applied as the light source, the excitation of catecin-molecules is out of question.

** Transparency of ordinary glass for infra-red rays of comparatively short wave-lengths was proved by W. Coblentz: Investigation of Infra-red spectra, Part III, p. 65.

Experimental.

(1) Absorption spectrum of Diethylenediamine-monoammonio-monochloro-cobaltic bromide. 1/100 Mol. aqueous solution of the cobaltic complex salt was prepared and its absorption spectrum was photographed in using a quartz spectrograph of Adam-Hilger; the absorption curve was then made according to the Hartley-Baly system. As was mentioned in Fig. 1, it contains two wide bands at $\lambda = 5000$ Å and $\lambda = 3640$ Å, both of which lie in the spectrum region transmitted by the green filter.

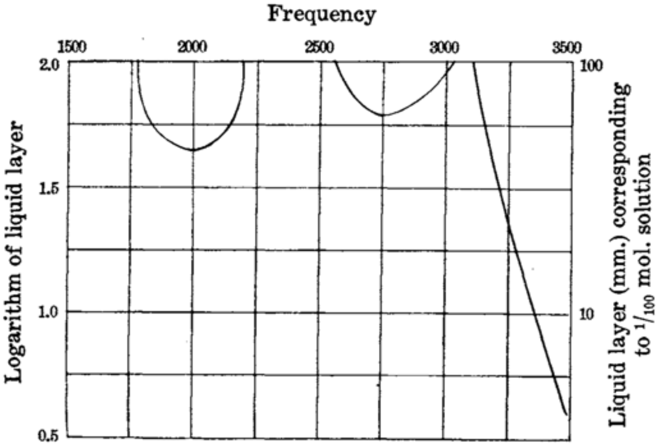

Fig. 1. Absorption curve of [Co $\underline{en}_2$ NH_3Cl] Br_2

(2) Oxidation of catechin by [Co $\underline{en}_2$ NH_3Cl] Br_2 under various colour filters. The procedure of this experiment and the apparatus used were quite the same as in the case of our recent investigation on asymmetric oxidation⁽¹⁾: catechin (1/250 mol solution) was mixed with the complex salt (1/500 mol solution) in the presence of the phosphate buffer (PH = 7.5) in the reaction bulb of Warburg's apparatus. The pressure depressions in the course of each reaction were given in Table 1.

Table 1.

Time (hour)	Colourless filter	Ruby glass	Green glass	$CuSO_4$-Sol.
0	0.00	0.00	0.00	0.00
1	0.10	0.08	0.81	0.49
2	0.20	0.09	−0.61	−0.30
3	0.65	0.31	−0.31	−0.35
4	0.98	0.87	+0.09	+0.13

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(1) Loc. cit.

Table 1.—(*Concluded*)

Time (hour)	Colourless filter	Ruby glass	Green glass	$CuSO_4$-Sol.
5	1.59	1.68	0.39	0.50
6	2.06	2.21	0.93	1.22
7	2.82	3.10	1.13	1.78
8	3.70	3.91	1.88	2.50
9	4.94	4.89	2.63	3.01
10	5.43	5.56	2.97	3.81
11	6.30	—	4.06	—
12	6.84	6.57	4.64	—
13	6.87	6.90	5.62	5.21
14	7.94	7.34	6.16	5.89
17	8.39	8.21	7.39	6.89
19	8.55	8.70	7.84	7.35
20	8.78	9.04	7.89	7.75
21	9.03	9.04	8.25	7.93
22	9.36	9.27	8.51	8.21
23	9.44	9.51	8.73	—
25	9.36	9.70	8.90	—

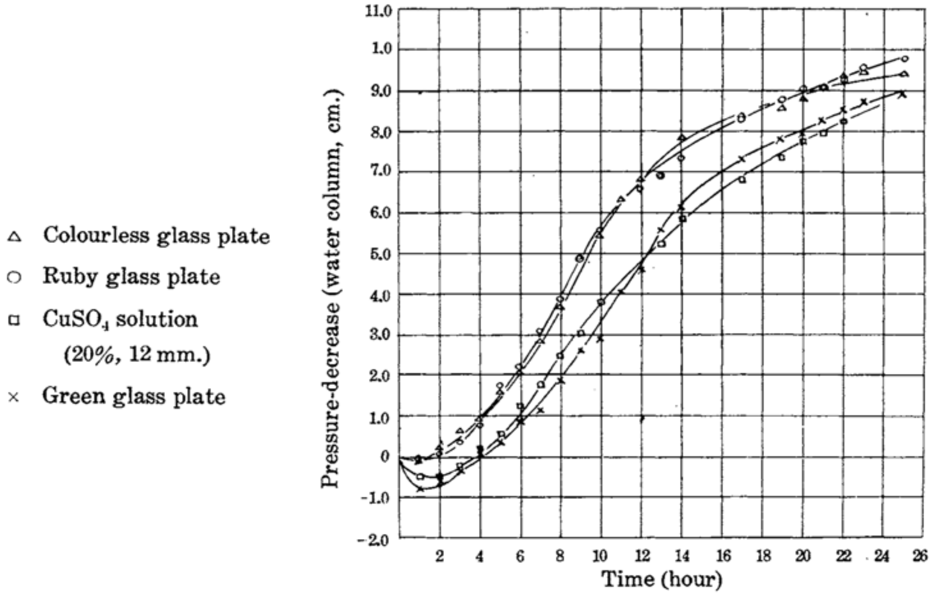

Fig. 2.

In the experiments above described, we observed, at the earlier stages of the oxidation reaction, slight increases of pressure in the apparatus; this inexplicable phenomanon has never been observed in our recent studies on asymmetric oxidation and will be left to later investigation.

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