

LXXXVII.—*The Absorption Spectra of Permanganates.*

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IN connexion with the hydrolysis of complex molecules of salts and the subsequent chemical changes which are increased or accelerated by light, I may refer to the experiments of Mr. J. E. Purvis on "The influence of dilution on the colour and the absorption spectra of various permanganates" (*Proc. Camb. Phil. Soc.*, 1909, 15, 111).

Experiments were made on potassium, zinc, and barium permanganates containing in 1000 c.c. of distilled water 0.316, 0.262, and 0.375 gram of the respective salts. They were each examined through cells 5 mm., 154 mm., and 310 mm. thick, each solution containing the same quantity of permanganate, the comparative solutions being made by diluting the strongest one 30.8 and 62 times respectively. The five bands measured by Lecocq de Boisbaudran were photographed, and the paper is illustrated by excellent photographic reproductions of the spectra, which show with distinctness only three of the bands.

"The explanation which seems to account for the changes is that the dissociating force of the water slowly acted on the dissolved permanganates, so that the ionic condition of $\overset{+}{R}$ and $\overset{-}{MnO_4}$,

where $\overset{+}{R}$ represents the metallic ion, broke down. One may imagine that the $\overset{-}{MnO_4}$ ion undergoes further dissociation into MnO_3 and O, or into MnO_2 and O_2 . In such dilute solutions the tension between the molecules of water surrounding the ions must have been very considerable, and it may have been so great as to destroy the $\overset{-}{MnO_4}$ condition, so that further changes took place which became visible in changes of colour, in changes in the width of the bands, and in the liberation of oxygen; and these changes would be accelerated by the vibrations of light."

"The intermediate stages of the changes might be represented by the narrowing of the bands 1, 2, and 3, and the widening of the bands 4 and 5, and these might correspond to changes of the $\overset{-}{MnO_4}$ ions into MnO_3 and O ions."

Such is the author's view. I venture to suggest that a simpler explanation is that which I have given in the case of nitrates which form basic salts, and in particular thorium nitrate (Trans., 1903, **83**, 221). A similar change also occurs in manganese nitrate and, as I shall show, in manganese sulphate.

In dilute solution the permanganates are hydrolysed and then decomposed into a colloidal solution of manganic hydroxide, $MnO(OH)_2$, and free oxygen. This action occurs even when the solutions are made in darkness and preserved in the dark. The most striking change seen in the spectra is a greatly increased general absorption, that is, a shortening of the transmitted rays. With solutions preserved in darkness it is apparently proportional to the dilution, but the effect of sunlight greatly increases the decomposition. The narrowing of the bands $\lambda\lambda$ 546 and 524, and the widening of those at $\lambda\lambda$ 504, 486, are easily explained by the decomposition having diminished the quantity of the permanganate or permanganic acid, and therefore weakened the bands and increased the quantity of the hydroxide, $MnO(OH)_2$, in colloidal solution; this has greatly extended the general absorption until it in part overlies the more refrangible of the bands. The absorption bands of permanganates are not characterised by sharpness; they have a hazy indistinctness, with no definite boundary lines such as are commonly seen in uranium, didymium, and erbium absorption spectra.

Owing to these properties, if the light is not diminished in intensity but the permanganate is reduced in quantity, the intensity of the bands will be diminished, and this will cause a reduction in their width. If, however, the intensity of the transmitted light is diminished, the reverse effect will be seen in an increased width of the bands. The intensity of the light is not diminished so far

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down into the green as λ 524, but the colloidal solution of the hydroxide, $\text{MnO}(\text{OH})_2$, not only extends the complete absorption in the direction of the bands, but also enfeebls the transmitted rays by a partial absorption extending to λ 504.

Hence, two of the bands in the less refrangible rays are narrower, and two in the more refrangible rays are broader, than in the unaltered solutions.

The observation is recorded that the stronger solutions appear to have the bands shifted towards the red, and this shift appeared to decrease with increased refrangibility of the absorbed rays. "In order to explain the different positions of the bands of the different solutions, the observations of H. Becquerel (*Compt. rend.*, 1886, 102, 106) show that such differences depend upon the concentration; the greater the concentration, the greater the shift of the bands towards the red end of the spectrum." This appears to offer no explanation of the cause of the shifting. If, however, we state that the concentrated solution is mainly a solution of the salt, and that dilution causes hydrolysis, the shift of the edge of the band to a more refrangible group of rays is precisely what might be expected by the conversion of barium permanganate into hydrogen permanganate; furthermore, we should expect the shift be of greater extent in the case of the barium salt than in that of the zinc permanganate, and from an inspection of the photographs this appears to be the case. Measurements were not made by Purvis; the figures are taken from Lecocq de Boisbaudran's "Spectres Lumineux." From the very nature of the bands they could not be measured with the precision desirable even with the dispersion of calcite prisms, owing to their indefinite character. This can be seen by comparing the photographs taken by Purvis No. 8 with No. 5; the former appears to be stronger than the latter, the bands being broader and more distinct, though they both represent solutions of the same salt of the same concentration, prepared and kept in darkness.

Manganese Sulphate.—Similar observations were made on this salt. A quantity of 4 kilograms was prepared in the highest degree of purity; it contained no trace of any other metallic base, and was perfectly neutral. The colour of the crystals was a delicate pale pink; a normal solution made with distilled water had a similar colour. The solution kept in a stoppered bottle passed through the following changes in colour on keeping. The pink became paler, the solution then became colourless, the colourless solution gradually assumed a pale yellow, the yellow gradually deepened to an amber tint. The disappearance of the pale pink was caused by the pale yellow, at first neutralising the violet and blue rays, which

being the complementary colours were freely transmitted; the unabsorbed green rays neutralise the red, thus constituting a colourless solution.

When the green rays had overpowered the pink, the yellow began to be visible. It must be borne in mind that the absorption phenomena are complicated by the admixture of an excess of white light, but this colour-change constantly occurs in pure solutions of the salt. In the original solution a narrow and well-defined absorption-band was photographed, which became obscured, and disappeared as the yellow colour developed; and this eventually became of a pale brown tint. For the explanation of the colour-changes we must admit that hydrolysis and oxidation are producing the colloidal hydroxide, $\text{MnO}(\text{OH})_2$. I have recorded the similar change in a normal solution of manganese nitrate, which led to the formation of a brown precipitate of manganic hydroxide.

The Absorption Band.—A normal solution of the salt, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, was examined through a column of liquid 200 mm. long. A general absorption enfeebles the rays as far as λ 3860, with a total absorption approximately as far as λ 3290; a transient absorption band lies between a broad air-line, λ 4025.3, and another air-line, very sharp and strong, λ 3995; there is a feeble extension of the band to λ 3952. The band overlaps a sharp lead-line, λ 4019.8, but only weakens without obscuring it. The absorption is therefore but feeble, and it is apparently caused by the oxidation of the solution. It indicates the progress of a chemical reaction, and the band disappears when the reaction is complete.

Note.—Since the foregoing observations were prepared for publication in February, 1911, a paper by T. R. Merton (Trans., 1911, 99, 637) has appeared with almost the same title.

It records careful measurements of the most conspicuous absorption bands in solutions of various permanganates in different liquids, including a solid solution of potassium permanganate in potassium perchlorate. The measurements of the maxima of absorption only are given, and all description of the nature of the bands as seen in the different solvents has unfortunately been omitted. Nevertheless, the author's conclusion is quite justified in respect to the general nature of the absorption being due to the atomic grouping, MnO_4 , which is influenced very little by the cation or by the extent of dissociation of the salt.

A very remarkable difference, however, is to be observed between the measurements of the bands in the solid solution and those in the liquids, which leads to a question whether they are the same bands shifted towards the violet end of the spectrum.

Having made a careful comparison of the figures, I have arrived at the conclusion that the bands in the solid solution are shifted into a region of less refrangible rays when the potassium permanganate is dissolved. This is highly suggestive of a state of combination of the solute with the solvent.

The following arrangement of the figures explains this. Let the solid solution and the solvents be numbered 1 to 11, and the bands be indicated in the order of the magnitude of the wave-lengths of the obscured rays by the letters *A*, *B*, *C*, selecting in every case the spectrum of potassium permanganate. By ascertaining the differences between the bands *A* and *B* and between *B* and *C* respectively in different solutions, the effect of the solvent is clearly shown, the probable accuracy of the figures being accepted as ± 3 Ångströms.

| | <i>A</i> . | <i>B</i> . | <i>C</i> . | Differences. | |
|-------------------------------------|------------|------------|------------|--------------|-------|
| (1) Solid solution | 5577 | 5345 | 5135 | 232 | 210 Å |
| (2) Solution in acetone..... | 5735 | 5496 | 5276 | 239 | 220 |
| (3) „ acetic anhydride | 5719 | 5480 | 5260 | 239 | 220 |
| (4) „ acetonitrile | 5718 | 5478 | 5258 | 240 | 220 |
| (5) „ methylacetate... | 5720 | 5480 | 5258 | 240 | 222 |
| (6) „ „ alcohol.. .. | 5747 | 5505 | 5285 | 242 | 220 |
| (7) „ „ ethyl „ .. | 5747 | 5503 | 5282 | 244 | 221 |
| (8) „ „ „ and amyl alcohol | 5747 | 5504 | 5280 | 243 | 224 |
| (9) „ „ ethylene glycol. | 5730 | 5484 | 5267 | 246 | 217 |
| (10) „ „ water | 5719 | 5477 | 5256 | 242 | 221 |
| (11) „ „ pyridine | 5738 | 5490 | 5271 | 248 | 219 |

It will be observed that the bands *A*, *B*, and *C* of No. 1, the solid solution, differ widely in position from the three corresponding bands in all the other solutions, although all these agree fairly well; the difference between No. 1 and all the other numbers

for the band *A*, lies between 142 and 172 Å.

„ „ *B*, „ „ 132 „ 160

„ „ *C*, „ „ 121 „ 150

The question arises whether the bands of No. 1 are really the bands corresponding to *A*, *B*, and *C* in the liquids, or whether they are not three more refrangible bands. This can be solved by the differences, for in the latter case the band *A* of No. 1 would correspond with band *B* of No. 2, etc., and the difference between *A* and *B* in the former would correspond with the difference between *B* and *C* in the latter, but it does not; it follows, therefore, that the action of the solvent on the solid solute changes the position of the bands into a region where the absorbed rays are of less refrangibility by 121 to 170 Ångströms, according to whether the band is *A*, *B*, or *C*.

As the author has remarked, it appears to be independent of the optical properties of the solvent.