

THE ABSORPTION SPECTRUM OF AQUEOUS CHLORINE AND HYDROGEN PEROXIDE VAPOUR.

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The extinction coefficients for gaseous chlorine have been accurately determined by v. Halban and Siedentopf¹ for the chief mercury arc lines, and Barratt and Stein² and Gillam and Morton³ have made measurements of the absorption of solutions of the gas in carbon tetrachloride, which show that the absorption spectrum in this solvent is approximately the same as that in the gaseous state.

The absorption of aqueous solutions have an especial interest on account of the thermal hydrolysis and photochemical reactivity of such solutions. According to E. S. Ssokolowa and P. I. Ssokolow⁴ the extinction coefficients of aqueous chlorine are, for the wave-length 436, 454, and 463 $m\mu$, approximately the same as those of the gas. This is in agreement with the earlier measurements of Allmand, Cunliffe and Maddison,⁵ who concluded that within the limits of their, admittedly,

¹ *Z. physik. Chem.*, 1922, **103**, 513.

² *Proc. Roy. Soc., A*, 1929, **122**, 582.

⁴ *J. Russ. Physic. Chem.*, 1930, **62**, 319.

⁵ *J. Chem. Soc.*, 1927, 655.

³ *Ibid.*, **124**, 604.

rather large experimental error there was no marked difference between the extinction coefficients of gaseous chlorine and its aqueous solution for the wave-lengths 436, 405, and 365 $m\mu$.

In the present work these measurements are repeated and extended so as to cover the whole spectrum between 420 and 220 $m\mu$. As, however, the thermal hydrolysis results in the production of hypochlorous and hydrochloric acids it was necessary to determine the magnitude of the corrections due to these substances. The degree of hydrolysis and consequently the concentrations of the acids present could be readily calculated from the values of the equilibrium constant given in Lewis and Randall's *Thermodynamics*, page 508. Owing to the very slight absorption of the chloride ion,⁶ no correction is necessary for the absorption of the hydrochloric acid. Hypochlorous acid on

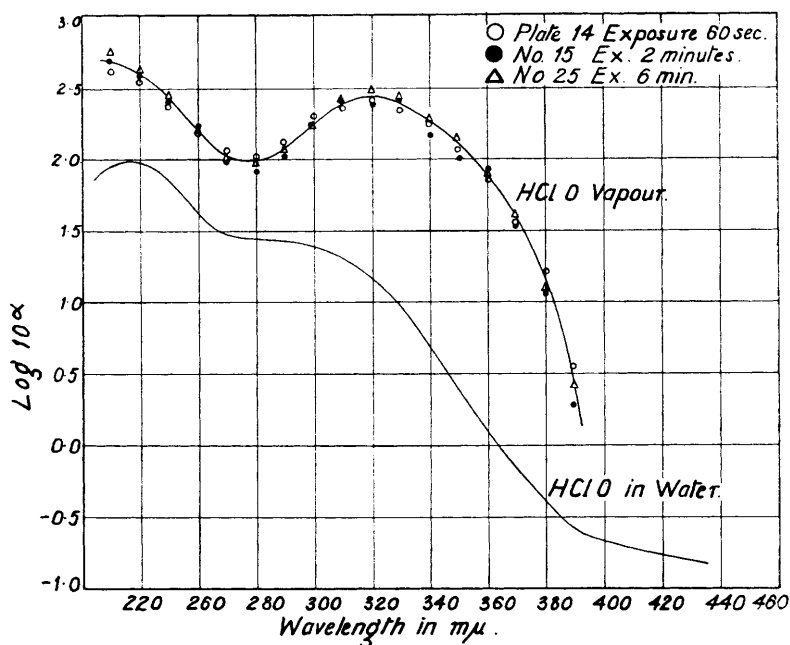


FIG. 1.

the other hand absorbs considerably throughout the spectral region investigated.

As the existing measurements on hypochlorous acid were neither extensive nor accurate enough, it was necessary as a preliminary to determine its absorption spectrum.

Hypochlorous Acid.—The acid was prepared by distillation of a mixture of bleaching powder, boric acid and water under reduced pressure, the distillate being redistilled from silver sulphate in order to remove traces of chloride. The approximately 0.2 *M.* solutions so prepared were diluted as required.

For the absorption measurements a Judd-Lewis sector photometer in conjunction with a Hilger E.2 quartz spectrograph and an iron spark

⁶ Frommers and Menschik; *Z. physik. Chem.*, 1930, **137**, 439.

was used. The points of equal density in the photographs were determined visually. The absorption cells were made up of drilled glass blocks over the ground plane-parallel ends of which crystal quartz plates were clamped. Although no cement was used, leakage was insignificant. Various depths of solution between 5.0 and 0.1 cm. were used. The reflection and other light losses were balanced by cells of similar depth filled with water. Transmissions greater than 50 per cent. were not used in order to avoid errors due to small differences in the characteristics of the cells. The concentrations were determined iodimetrically.

The mean results of these measurements are shown in Fig. 1 in which logarithms of the decadic extinction coefficients are plotted against the wave-length. No dependence of the extinction coefficient upon the concentration could be detected within the concentration range of 0.017 — 0.15 *M*.

Chlorine Water.—For the preparation of the chlorine water both commercial chlorine taken direct from a cylinder of the liquefied gas and

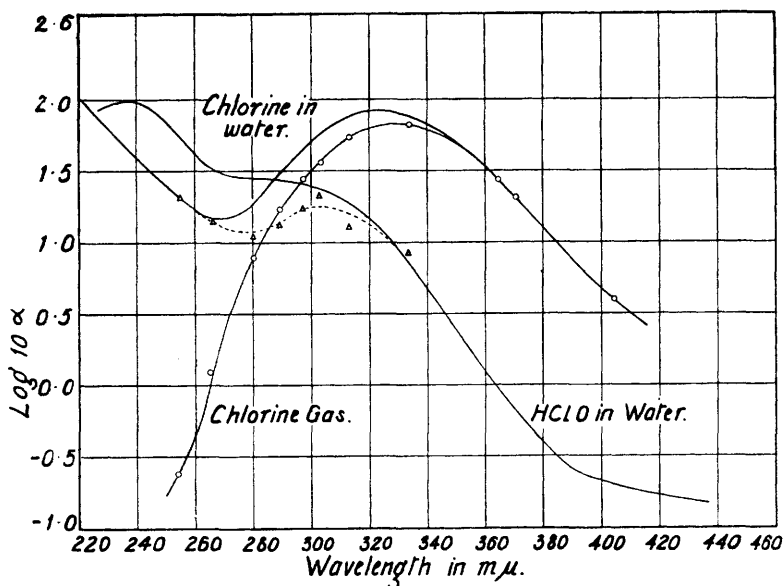


FIG. 2.

chlorine purified by washing with water, liquefaction and distillation were used. The purified chlorine gave somewhat lower values of the extinction coefficient particularly at shorter wave-lengths where the correction for the hypochlorous acid formed by the hydrolysis is of most importance.

In order to avoid concentration changes, the chlorine solutions were prepared by passing the chlorine through water contained in a special all-glass storage vessel. From this vessel the solution could be siphoned out either into the absorption cell or into a special pipette designed by Mr. H. N. Ridyard and K. W. Young for accurate measurements on chlorine solutions. The air replacing the chlorine water removed, passed through two bubblers containing solution of the same strength as that in the main vessel.

The concentrations of the chlorine-water was determined both immediately before and immediately after filling the absorption cell, the mean value being taken as that of the solution in the cell.

The extinction coefficients of the unhydrolysed chlorine were calculated from the expression

$$\log_{10} \frac{I_0}{I} = d(\alpha_{\text{Cl}_2}[\text{Cl}_2] + \alpha_{\text{HOCl}}[\text{HOCl}])$$

in which α_{Cl_2} and α_{HOCl} are the extinction coefficients of Cl_2 and HOCl respectively, I_0 and I respectively the incident and transmitted light intensities, and d the thickness of the absorbing layer of solution.

As the degree of hydrolysis, and consequently the correction for the absorption of hydrochlorous acid increases with the dilution, concentrations of less than 0.04 M . could not be used for quantitative measurements. The results obtained with the purified chlorine are plotted in Fig. 2.

Since the absorption spectrums of aqueous hypochlorous acid might differ considerably from that of the vapour, and in particular since discontinuous absorption if it occurs could only be detected in the vapour phase, the absorption of the vapour was investigated. At the same time the absorption of hydrogen peroxide vapour was also redetermined as it seemed probable that the work of Urey, Dawsey and Rice⁷ was in error, since their results for aqueous solutions differ considerably from the concordant results of several other workers.⁸ No indication of any discontinuity in the absorption of hypochlorous acid vapour could be detected between 230 and 390 $m\mu$, using a Hilger E. 2 Spectrograph.

Hydrogen Peroxide and Hypochlorous Acid Vapours.—Since neither of these substances can be obtained at a high concentration in the vapour phase, it is necessary to employ a long absorption tube if the absorption measurements are to be reliable. A translucent silica tube 10 metres in length and 2.5 cm. in diameter with fused on transparent end plates, heated electrically to about 45° C. was used. The hypochlorous acid vapour was obtained from aqueous solutions prepared by the method already described and the peroxide vapour from redistilled Merck's "Perhydrol."

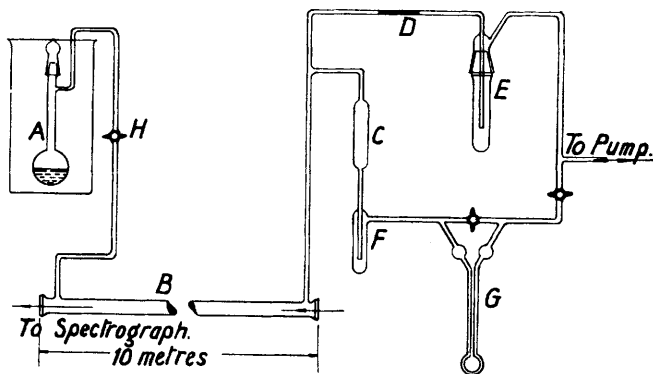


FIG. 3.

To one end of the absorption tube B (Fig. 3) was sealed a quartz flask A, containing a solution of the vapour to be investigated. During absorption measurements the vapour was distilled through B into the liquid air trap E, a convenient pressure being maintained in B by the capillary D and control of the tap H. A "Hyvac" pump continually removed permanent gas. In order to measure the pressure in B a narrow bore lead was taken from one end of B to the manometer G. Peroxide vapour was prevented from reaching the manometric liquid by manganese dioxide heated to 100° C. contained in the bulb C, while the water vapour initially present or formed by the decomposition of the peroxide was frozen out in the trap F, so that only oxygen reached the manometer. With

⁷ Urey, Dawsey and Rice; *J.A.C.S.*, 1929, **51**, 1371.

⁸ Henri and Wurmser; *C.R.*, 1913, **156**, 1012; Rieche and Lederle, *Ber.*, 1929, **62**, 2573; Allmand and Style, *J. Chem. Soc.*, 1930, 596.

hypochlorous acid, C was replaced by a capillary leak open to the atmosphere in order to supply the gas to operate the manometer.

After each exposure the condensate in the trap E was melted and the molal fraction of peroxide or hypochlorous acid determined by the usual analytical methods. The temperature and total pressure in the absorption tube being known, the concentrations of the absorbing vapours could be readily calculated. These lay between 1 and 4×10^{-6} gm. mols./litre with hypochlorous acid and between 5×10^{-5} and 5×10^{-6} with hydrogen peroxide.

A hydrogen discharge between stainless steel electrodes in a water-cooled silica tube served as the light source. Before entering the absorption tube the light was rendered approximately parallel by the sector box lens system of a dismantled Judd-Lewis sector photometer. The absorption of the peroxide vapour was determined by taking pairs of photographs with the same time of exposure without moving the photo-

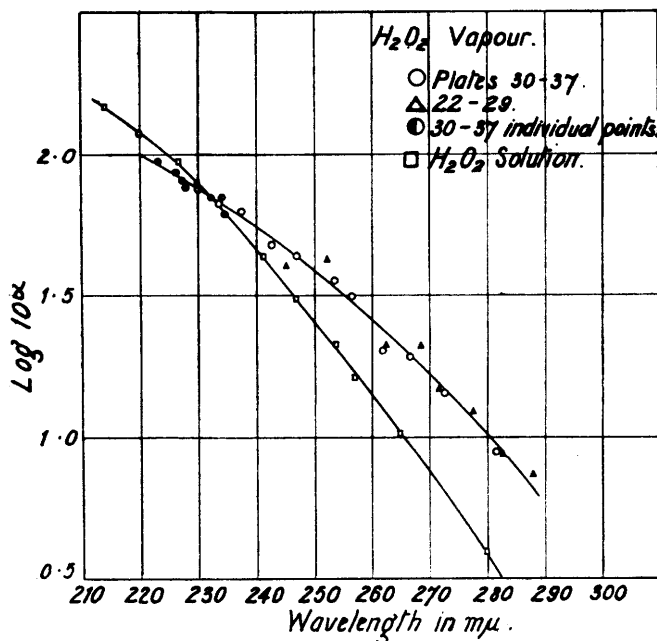


FIG. 4.

graphic plate but with different adjacent portions of the slit of the spectrograph exposed, one with the tube evacuated (the tap H being closed) and the sector set to reduce the light intensity by a known amount, and the other with peroxide vapour flowing through the tube and the sector adjusted to give the maximum transmission. The match points were determined visually. The accuracy to this method was checked by determining the extinction coefficients of chlorine, values within 5 per cent.

of those given by v. Halban and Siedentopf being obtained.

The instability of hypochlorous acid and the weak absorption usually obtained with it necessitated the adoption of a different procedure with this substance.

A calibration series of spectra was photographed through the evacuated tube with constant time of exposure, but with the sector adjusted to give different transmissions. Photographs were then taken with the same exposure but with hypochlorous acid vapour flowing through the tube and the sector set to give the maximum transmission. The absorption of the vapour at a number of wave-lengths was then found by comparing the densities of the photographs taken through the vapour with the calibration series by means of a recording micro-photometer.

The results for hydrogen peroxide are shown in Fig. 4 and the results from a few representative plates obtained with hypochlorous acid in Fig. 1.

Discussion.

Although, as can be seen from the scattering of the extinction coefficients of gaseous hypochlorous acid, no great accuracy can be claimed, there can be no doubt that there is a very considerable difference between the absorption of this substance in the vapour and dissolved states. This difference cannot be ascribed to either chlorine monoxide or chlorine dioxide, since the absorption in no way resembles that of the monoxide,⁹ and the very easily detectable bands of the dioxide were entirely absent from all plates used for measurement. The dioxide bands did, however, sometimes appear if the hypochlorous acid solution was not freshly prepared. The very marked depression of the transition probability on passing from the vapour to the dissolved state is rather exceptional since chlorine is scarcely affected at the longer wave-lengths, and with hydrogen peroxide the effect of dissolution seems to be to simultaneously increase the maximum absorption and make the band narrower. The mean time of contact of the vapour with the heated tube was only of the order of 5 seconds, but no attempt was made to keep it constant from exposure to exposure, so that the difference between solution and vapour can scarcely be accounted for by assuming that some 90 per cent. of the vapour decomposed during its passage through the absorption tube. The concentration of the condensate was moreover too great to allow of the assumption that any extensive decomposition had occurred. The large effect of the solvent may perhaps be due to the asymmetry of the hypochlorous acid molecule, and its consequent considerable interaction with the water dipoles.

The dissociation products which might be obtained from the hypochlorous acid molecule are: $\text{OH} + \text{Cl}$ (either or both being excited), requiring 55 Cals. for unexcited products, $\text{HCl} + \text{O}({}^3P)$, requiring 57 Cals., $\text{HCl} + \text{O}({}^1D)$ requiring 102 Cals. and $\text{H} + \text{ClO}$ requiring 109 Cals., if the heat solution of hypochlorous acid is taken as 10 Cals. and the heat of dissociation of ClO is 50 Cals.¹⁰ Either of the two first of these might be produced by light absorption in the longer wave-length band. The failure to detect the presence of any discontinuity in the absorption even at the wave-length where the extinction coefficient is a minimum ($\lambda \sim 277 \text{ m}\mu$) excludes any process requiring more than 102 Cals. from responsibility for the absorption at shorter wave-lengths. Dissociation into $\text{H} + \text{ClO}$ can thus be left out of account unless this band is not simple, as it appears to be. $\text{HCl} + \text{O}({}^1D)$ remain, however, just possible.

The maximum of the second band lies outside the region covered by these measurements, but from the general trend of the curve might be expected to occur at about $210 \text{ m}\mu$, giving about 47 Cals. as the energy separation of the two maxima. This approximates to the difference between the two oxygen terms ${}^1D - {}^3P = 45$ Cals. Notwithstanding this apparent agreement the available evidence scarcely justifies the assignment of any one of the three possible dissociation processes to either band.

The effect of water upon the absorption of chlorine is zero within the experimental error for wave-lengths between 350 and $420 \text{ m}\mu$.

⁹ Goodeve and Wallace, *Trans. Faraday Soc.*, 1930, **26**, 254. Also ref. 10.

¹⁰ Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, B, 1931, **15**, 127.

At shorter wave-lengths, however, there is an increase in the absorption culminating in the appearance of a new band below $270\text{ m}\mu$, the maximum of which is not attained within the limits of our measurements.

A similar but more intense change in the absorption has been found on dissolution in strong aqueous hydrochloric acid (4 to 10 molar), when a very intense absorption sets in below $290\text{ m}\mu$, the absorption at longer wave-lengths remaining meanwhile similar to that of the gas. If the hydrochloric acid contained hydrobromic acid the long wave-length maximum shifted to $380\text{ m}\mu$, the position of the maximum of bromine chloride in carbon tetrachloride.¹¹ According to the data of Forbes and Fuoss¹² the chlorine would have reacted almost completely to form bromine chloride under our conditions. The absorption obtained with the solutions containing hydrobromic acid was very similar to that of BrCl_2^- excepting that the absorption at shorter wave-lengths found by us was much stronger than that reported by Gilbert, Goldstein and Lowry.¹³ This difference is readily accounted for if the complex ion is considerably dissociated if a large excess of chloride ion is not present.

By analogy the ion Cl_2^- is presumably responsible for the absorption obtained with chlorine in hydrochloric acid solution, and further, the difference between the absorption of gaseous chlorine and its aqueous solution (which is indicated by the dotted curve of Fig. 2) may be ascribed to the ion Cl_2OH^- or perhaps the molecule HCl_2OH . Though possibly merely a coincidence it is worth noting that this difference rather closely resembles the absorption of hypochlorous acid vapour (Fig. 1).

In view of the experimental methods employed, it would seem that the present values of the extinction coefficients of hydrogen peroxide are to be preferred to those of Urey, Dawsey and Rice.

Summary.

The absorption spectra of aqueous chlorine and hypochlorous acid solutions and of the vapours of hypochlorous acid and hydrogen peroxide have been investigated.

The interpretation of the observations is discussed.

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¹¹ Gillam and Morton, *Proc. Roy. Soc., A*, 1929, **124**, 604.

¹² Forbes and Fuoss, *J.A.C.S.*, 1927, **49**, 142.

¹³ *J. Chem. Soc.*, 1931, 1092.