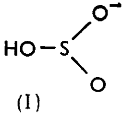
741. *Ultraviolet Absorption Studies of the Bisulphite–Pyrosulphite Equilibrium.*

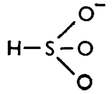
By R. M. GOLDING.

Four species are suggested to explain the ultraviolet absorption spectra of bisulphite at various concentrations: the $S_2O_5^{2-}$ ion ($\lambda_{max.} = 255$ mμ, log $\varepsilon = 3{\cdot}60$); the HSO_3^- ion ($\lambda_{max.} = 215$ mμ, log $\varepsilon = 1{\cdot}78$); the $HO{\cdot}SO_2^-$ ion ($\lambda_{max.} = 205{\cdot}2$ mμ, log ε apparent $= 2{\cdot}75$); the equilibrium $2HSO_3^- \rightleftharpoons S_2O_5^{2-}$, which is confirmed; $K = [S_2O_5^{2-}]/[HSO_3^-]^2 = 7 \times 10^{-2}$ mole^{-1}.

LORENZ and SAMUEL[1] measured the ultraviolet absorption spectrum (400—220 mμ) of bisulphite at two concentrations, N- and N/10-sodium hydrogen sulphite. Both spectra had a peak at 255 mμ, which did not obey Beer's law for the HSO_3^- ion. Schaefer *et al.*[2] postulated two isomeric forms of bisulphite, (I) and (II). To attempt to explain the ultraviolet spectrum of bisulphite solutions they introduced a "time-dependent equilibrium" between the two isomeric forms (I) and (II). From Raman and ultraviolet studies, Simon *et al.*[3] have shown that the equilibrium of the bisulphite solution is not "time dependent," confirming the earlier work of Baly and Bailey.[4] The latter workers compared conductance measurements on sulphite solutions with ultraviolet absorption measurements. From their ultraviolet absorption results, the 255 mμ peak was assigned to the $S_2O_5^{2-}$ ion.



(I)



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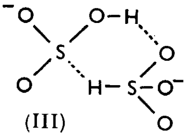

(III)

In this paper the 255 mμ peak is first shown to be due to a compound containing two

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[1] Lorenz and Samuel, *Z. phys. Chem.*, 1931, *B*, **14**, 219.

[2] Schaefer, Niggemann, and Kohler; *Z. Elektrochem.*, 1915, **21**, 181; Schaefer and Kohler, *Z. anorg. Chem.*, 1918, **104**, 212.

[3] Simon and Waldmann, *Z. anorg. Chem.*, 1955, **281**, 113, 135; 1956, **284**, 36, 47; Simon, Waldmann, and Steger, *ibid.*, 1956, **288**, 131.

[4] Baly and Bailey, *J.*, 1922, **121**, 1813.

sulphur atoms, then that it is due to the $S_2O_5^{2-}$ ion and not to $HS_2O_5^-$ or $H_2S_2O_5$. At low concentrations of bisulphite the only peak is at 205·2 mμ, which is shown to be due to a compound containing one sulphur atom and is assigned to the $HO{\cdot}SO_2^-$ isomer of bisulphite. As the total sulphur concentration is increased, the 205·2 mμ peak does not continue to obey Beer's law but the wavelength maximum shifts towards approximately 215 mμ. At high concentrations the 215-mμ absorption obeys Beer's law for a compound containing one sulphur atom, and the HSO_3^- isomer of bisulphite is assigned to this peak. The shift of the peak from 205·2 mμ to 215 mμ is explained by a hydrogen-bonding mechanism.

EXPERIMENTAL

All the ultraviolet absorption spectra were measured on a Beckman D.U. spectrophotometer, and at the low wavelengths stray light was allowed for, by standardisation with potassium dichromate. The cells used were of 1 cm. or 1 mm. path length depending on the concentration used, and the spectra were measured at 20°.

Potassium pyrosulphite was prepared by bubbling sulphur dioxide through a saturated solution of the carbonate until the solution was acidic. The white solid was dried and identified as pyrosulphite by *X*-ray powder pattern.[5] Just before a solution was made from the prepared pyrosulphite its purity was determined by titrating a solution with a standard iodate solution.[6]

Results.—The ultraviolet absorption spectra of solutions of sulphur dioxide at various pH values from 1 to 10 were measured at low total sulphur concentrations (less than 3×10^{-3}M). There were three characteristic ultraviolet spectra: (1) below pH 2, adjusted with hydrochloric acid. (The pH was measured on a Cambridge pH meter; the adjusted solution was halved, and one portion used to determine the pH and the other portion to measure the spectrum: this prevented contamination from the pH electrodes which would interfere with the absorption spectra.) (2) pH 3·5—5·5, adjusted with hydrochloric acid; (3) above pH 8, borate buffer (checked by pH meter). These are shown in Fig. 1 and are assigned as (1) sulphur dioxide in water, (2) bisulphite, and (3) sulphite. All the spectra subsequently recorded in this paper were measured in the pH range 3·5—5·5, as only the bisulphite ions are considered. Table 1 shows that the ion causing the absorption at 205·2 mμ obeys Beer's law for a species containing one sulphur atom at low concentrations (below 3×10^{-3}M): $[HSO_3^-]$ is the bisulphite concentration, D the optical density, and E the molecular extinction.

TABLE 1.

$[HSO_3^-]$	$9{\cdot}6 \times 10^{-4}$	$1{\cdot}53 \times 10^{-3}$	$2{\cdot}31 \times 10^{-3}$	$2{\cdot}77 \times 10^{-3}$	$6{\cdot}00 \times 10^{-3}$	$1{\cdot}48 \times 10^{-2}$	$3{\cdot}70 \times 10^{-2}$
D	0·056 *	0·820 †	0·125 *	1·57 †	0·268 *	0·450 *	0·500 *
10^2E ...	5·84	5·36	5·41	5·66	4·46	3·02	1·35

* 1 Mm. cell. † 1 Cm. cell.

The extinction coefficient of the bisulphite species at low concentrations is $5{\cdot}62 \times 10^2$ (from slope of the plot of D against total sulphur concentration). This species with $\lambda_{max.}$ at 205·2 mμ will be labelled bisulphite (I).

As the bisulphite concentration is increased, a peak at 255 mμ begins to appear. In the following expressions let $D = \varepsilon dc$ where ε = molecular extinction coefficient, d = path length, and c = concentration of absorbing species. If the sulphur species is mainly present as an S form (which has been shown for low concentrations) and in a small extent as an S_n form, with the two forms in equilibrium, then $nS \rightleftharpoons S_n$ and $[S_n] = K[S]^n$, where K is the equilibrium constant, therefore $D = K\varepsilon d[S]^n$ if the measured absorption at the particular wavelength is due to the S_n species. As

$$\log D = n \log [S] + \log K\varepsilon d \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

a plot of log D against log [S] determines the value of n, and such a plot for the 255 mμ peak yields a straight line over the entire concentration range measured. From the graph (Fig. 2) the value for n is 2. The species at 255 mμ therefore contains two sulphur atoms.

Solutions made from sodium sulphite and from potassium pyrosulphite, with adjustment of the pH in each case gave the same ultraviolet absorption spectra for varying concentrations

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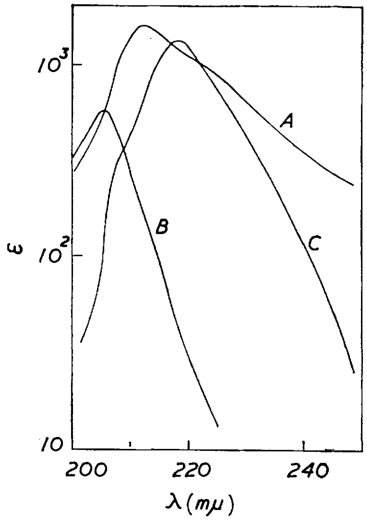
[5] A.S.T.M. cards.

[6] Kolthoff and Belcher, "Volumetric Analysis, Vol. III," Interscience Publishers Inc., New York, 1957, p. 451.

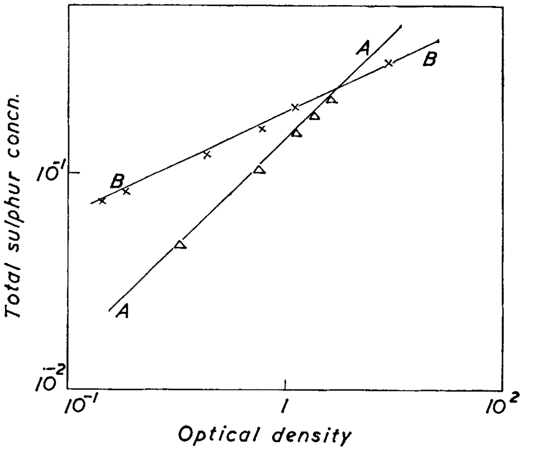
(Table 2). This establishes a direct equilibrium between bisulphite and pyrosulphite with no " time dependence." Hence it is established that (1) the 255 mμ peak is due to a species containing two sulphur atoms and (2) there is a simple equilibrium between bisulphite and a pyrosulphite species which absorbs at 255 mμ.

FIG. 1.



A pH <2. *B* pH 3·5—5·5. *C* pH >8.

FIG. 2.



A 215 mμ. *B* 255 mμ.

The bisulphite species is labelled HS* for the present. The three possibilities for the bisulphite–pyrosulphite equilibria are

$$2\mathrm{HS}^* \rightleftharpoons \mathrm{S_2O_5}^{2-} + \mathrm{H_2O} \text{ and } [\mathrm{S_2O_5}^{2-}]/[\mathrm{HS}^*]^2 = K_1 \quad \ldots \quad (1)$$

$$2\mathrm{HS}^* + \mathrm{H}^+ \rightleftharpoons \mathrm{HS_2O_5}^- + \mathrm{H_2O} \text{ and } [\mathrm{HS_2O_5}^-]/[\mathrm{HS}^*]^2[\mathrm{H}^+] = K_2 \quad \ldots \quad (2)$$

$$2\mathrm{HS}^* + 2\mathrm{H}^+ \rightleftharpoons \mathrm{H_2S_2O_5} + \mathrm{H_2O} \text{ and } [\mathrm{H_2S_2O_5}]/[\mathrm{HS}^*]^2[\mathrm{H}^+]^2 = K_3 \quad \ldots \quad (3)$$

These equilibrium equations can be summarised as

$$[\mathrm{S_2}^*]/[\mathrm{H}^+]^{n-1}[\mathrm{HS}^*]^2 = K_n \quad \ldots \quad (4)$$

Where $n = 1$, $\mathrm{S^*}_2 = \mathrm{S_2O_5}^{2-}$; where $n = 2$, $\mathrm{S^*}_2 = \mathrm{HS_2O_5}^-$; and where $n = 3$, $\mathrm{S^*}_2 = \mathrm{H_2S_2O_5}$.

Let S be the concentration of total sulphur, then

$$S = [\mathrm{HS}^*] + 2[\mathrm{S_2}^*] = ([\mathrm{S_2}^*]/[\mathrm{H}^+]^{n-1}K_n)^{\frac{1}{2}} + 2[\mathrm{S_2}^*]$$

Substituting for HS* from equation (4), we have, at 255 mμ, $D = \varepsilon_n d\,[\mathrm{S_2}^*]$, therefore

$$S = (D/\varepsilon_n d\,[\mathrm{H}^+]^{n-1}K_n)^{\frac{1}{2}} + 2D/\varepsilon_n d$$

i.e.,

$$S/D = AD^{-\frac{1}{2}} + B \quad \ldots \quad (5)$$

where $A^2 = (\varepsilon_n d[\mathrm{H}^+]^{n-1}K_n)^{-1}$ and $B = 2/\varepsilon_n d$.

From equation (5) and the slope of the plot of S/D against $D^{-\frac{1}{2}}$, K_n and n may be evaluated, and from the intercept ε_n can be evaluated. Table 2 gives a summary of the various solutions measured at 255 mμ.

Inspection of Table 2 shows that the gradient of a plot of S/D against $D^{-\frac{1}{2}}$ [*i.e.*, equation (5)] is independent of pH and is a function of $[\mathrm{H}^+]^{n-1}$, $n = 1$. Hence, the species at 255 mμ is $\mathrm{S_2O_5}^{2-}$ and not $\mathrm{HS_2O_5}^-$ or $\mathrm{H_2S_2O_5}$. From a plot of S/D against $D^{-\frac{1}{2}}$ the value for A is found to be 0·1861. Since $n = 1$ and $d = 10^{-1}$, $\varepsilon K_1 = 288$. The intercept is about 5×10^{-3}, therefore ε is about 4×10^3. Since the intercept is small, a large error is inherent in the

TABLE 2.

Added as	S	D	$D^{-\frac{1}{2}}$	S/D	pH
Na_2SO_3	0·0735	0·142	2·655	0·518	4·12
$K_2S_2O_5$	0·0771	0·165	2·461	0·461	—
$K_2S_2O_5$	0·0802	0·181	2·35	0·444	4·05
$K_2S_2O_5$	0·0806	0·194	2·270	0·416	3·58
$K_2S_2O_5$	0·0917	0·228	2·098	0·402	4·60
$K_2S_2O_5$	0·1030	0·305	1·810	0·338	—
Na_2SO_3	0·1100	0·322	1·760	0·341	4·12
$K_2S_2O_5$	0·1201	0·424	1·537	0·2838	4·05
$K_2S_2O_5$	0·1209	0·422	1·540	0·2850	3·70
$K_2S_2O_5$	0·1289	0·490	1·428	0·2620	—
$K_2S_2O_5$	0·1358	0·528	1·378	0·2585	4·48
Na_2SO_3	0·1469	0·609	1·282	0·2410	4·17
$K_2S_2O_5$	0·1602	0·778	1·134	0·2060	4·02
$K_2S_2O_5$	0·1604	0·748	1·157	0·2142	4·55
Na_2SO_3	0·1835	1·000	1·000	0·1840	4·13
$K_2S_2O_5$	0·1930	1·184	0·918	0·1630	—
$K_2S_2O_5$	0·2002	1·200	0·931	0·1670	4·04
$K_2S_2O_5$	0·2009	1·227	0·904	0·1638	4·60
Na_2SO_3	0·2200	1·470	0·825	0·1500	4·24
$K_2S_2O_5$	0·2248	1·699	0·768	0·1320	—
$K_2S_2O_5$	0·2398	1·715	0·755	0·1398	4·05
$K_2S_2O_5$	0·2422	1·792	0·746	0·1356	4·50
$K_2S_2O_5$	0·3215	2·976	0·579	0·1080	—

molecular extinction. It can be shown that the theoretical maximum value of ε in any compound is about 10^4, but from the results, the intercept must be less than 10^{-2}, therefore ε is greater than 2×10^3. Consequently, approximate values of ε and K can be obtained as 4×10^3 and 7×10^{-2} mole^{-1}, respectively.

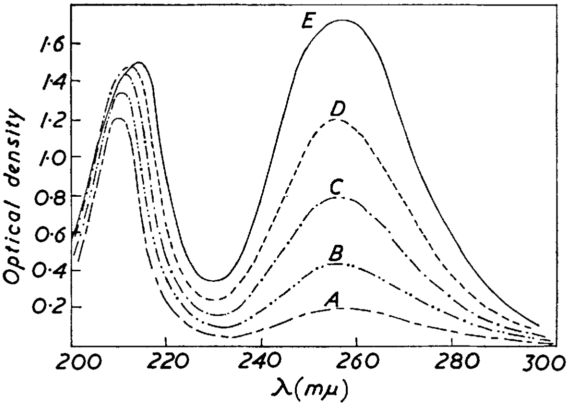


FIG. 3. Ultraviolet spectrum of HSO_3^-–$S_2O_5^{2-}$: 1-mm. cell, pH 4·05. Total sulphur concentration: *A*, 0·0802M; *B*, 0·1201M; *C*, 0·1602M; *D*, 0·2002M; *E*, 0·2398M.

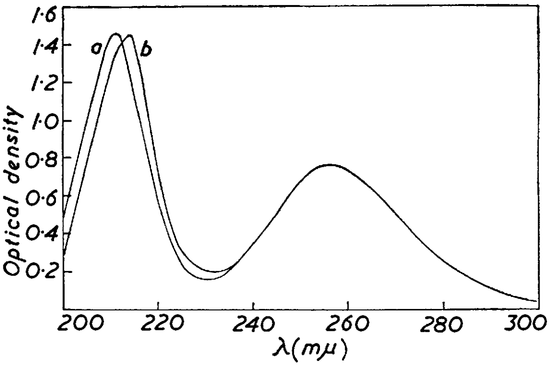


FIG. 4. *Plot of optical density against wavelength for constant sulphite concentration at various values of* pH.
(*a*) pH 4·05, 3·75, 3·50; (*b*) pH 4·60.

The next part of the spectrum to be explained is the 205·2 mμ peak. As was shown, below concentrations of 3×10^{-3}M the peak obeys Beer's law, but above this concentration the peak moves towards 215 mμ. This is shown in the graph (Fig. 3) for varying total concentration of sulphur but with pH constant at 4·05. Applying equation (*a*) we find that $n = 1{\cdot}00$ at 215 mμ. Hence the 215 mμ species is also a single-sulphur compound. The extinction coefficient is evaluated in Table 3, showing that Beer's law is obeyed at high concentration. Hence the

TABLE 3.

Bisulphite concn.	0·0802	0·1201	0·1602	0·2002	0·2398
D (1 mm. cell)	0·564	0·850	1·126	1·386	1·622
ε	70·1	70·8	70·2	69·2	68·0

extinction coefficient of the bisulphite species, which will be referred to as bisulphite (II), is 70 and its peak is at 215 mμ.

The oscillator strengths, f, are calculated for the bands at 205·2, 215, and 255 mμ by using the equation $f = 3{\cdot}64 \times 10^{-9}\int\varepsilon.d\nu$ obtained by Chako [7] for dilute solutions, *i.e.*, the refractive index of the solution is the same as for the solvent, water. The following Table is a summary of the oscillator strengths for the bands.

Band	205·2 mμ	215 mμ	255 mμ
Oscillator strength	$4{\cdot}6 \times 10^{-3}$ (apparent)	$9{\cdot}2 \times 10^{-4}$ (apparent)	$8{\cdot}3 \times 10^{-3}$

The pH does not affect the 255 mμ peak, but at high concentrations of bisulphite the 215 mμ peak is altered by pH changes (Fig. 4).

As before, let HS* represent the bisulphite ion. Consider the equilibrium

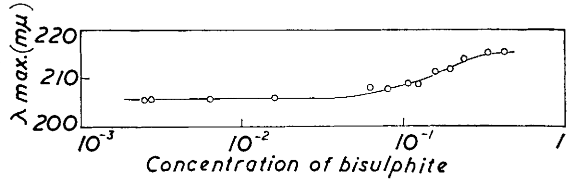
$$\mathrm{HS}^* \rightleftharpoons \mathrm{SO_3}^{2-} + \mathrm{H}^+ \text{ and } K = [\mathrm{H}^+][\mathrm{SO_3}^{2-}]/[\mathrm{HS}^*] = 10^{-7}$$

The equilibrium constant, K, is a concentration term obtained from Cuta *et al.*[8] at the appropriate ionic strength. For the SO_3^{2-} ion $\lambda_{\max.} = 218$ mμ and $\varepsilon_{\max.} = 1{\cdot}29 \times 10^3$. The greatest bisulphite concentration used in this work is 0·27M. For this concentration at pH 4·60 the SO_3^{2-} ion concentration will be approximately $1{\cdot}08 \times 10^{-3}$M, hence the optical density in a 1-mm. cell at 218 mμ due to the SO_3^{2-} ion is 0·140. Similarly at pH 4·00 the optical density due to the SO_3^{2-} ion in a 1-mm. cell is 0·035, which is negligible. Therefore, even at the greatest bisulphite concentrations used, the SO_3^{2-} ion has negligible effect on the bisulphite peak at pH 4. Decreasing the pH from 4·60 at constant high concentrations will alter the shape of the composite bisulphite peak towards the shorter wavelength as shown in Fig. 4, owing to the decrease of the SO_3^{2-} concentration.

DISCUSSION

Consider the two isomeric bisulphite species as postulated by Schaefer and Kohler.[3] The sulphur atom in species (I) has one available π-orbital whereas species (II) has no available π-orbital. The oscillator strength for the first transition depends on the coefficients of the π-combination in the first excited orbitals [9] and can be written as $f \propto h^2$, where h is the coefficient of the π-combination in the excited state. It can be seen that $h(\mathrm{I}) > h(\mathrm{II})$, therefore $f(\mathrm{I}) > f(\mathrm{II})$. Hence species (I) has the greater oscillator strength and will dominate the ultraviolet spectrum if both species are present in comparable amounts. This appears to be the case, as species (III) (see later) predominates at high concentrations. This would not be observed if one of the bisulphite species dominated. Since the major peak at low concentrations is at 205·2 mμ the $HO{\cdot}SO_2^-$ (species I) may be assigned to it. However, this peak will be made up of both species (I) and (II), and consequently the extinction coefficient will only be apparent.

FIG. 5.



Species (I) and (II) must be in equilibrium, as diluting a strong bisulphite solution shifts the wavelength from 215 mμ to 205·2 mμ, as shown in Fig. 5. A simple equilibrium (I) $\rightleftharpoons$ (II) would not give the shifting peak. At higher concentrations species (I) may tend to form a hydrogen bond with species (II), giving a six-membered ring (as III).

It has been postulated [10] that hydrogen bonding in the ultraviolet spectra of weak acids

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[7] Chako, *J. Chem. Phys.*, 1934, **2**, 645.

[8] Cuta, Beranch, and Pisechy, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1496.

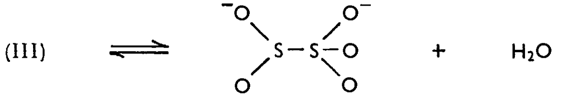
[9] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

[10] Forbes and Knight, *Canad. J. Chem.*, 1959, **37**, 334.

causes wavelength shifts due to concentration changes. Martin and Rossotti[11] have shown that for weak aliphatic acids the monomer is favoured at concentrations less than 5×10^{-2}M, and above this the complex appears. As the total sulphur concentration increases, hydrogen bonding becomes more favoured and species (III) is formed; consequently the concentration of species (I) is reduced. Hydrogen bonding to the sulphur atom in species (I) will greatly alter the π-orbital contribution to the first excited state of species (I), and consequently the extinction coefficient of bisulphite will decrease as the concentration increases. Hence the 215 mμ peak is due to species (III), but this may be considered as the form species (II) takes in solution at these concentrations.

Next consider the complete set of equilibria in bisulphite solutions:

(I) $\rightleftharpoons$ (II) low concentration (3×10^{-3}M)
(I) + (II) $\rightleftharpoons$ (III) high concentration (10^{-2}M)



Zachariasen[12] determined the crystal lattice of potassium pyrosulphite and the structure of the pyrosulphite group. Recent work by Lindquist and Mortsell[13] has confirmed the structure which has a C_1 symmetry with an S–S bond. The pyrosulphite ion has an S–S bond and S–O bonds and not an S–O–S configuration as suggested by Simon, Waldmann, and Steger.[3] They considered all the possible symmetry groups and although they finally assigned the symmetry group C_{2v} to the $S_2O_5^{2-}$ ion, their evidence is not complete. The Raman spectrum consists of 15 vibrations ($3n - 6$) which Simon *et al.* tabulated. For the symmetry group C_{2v}, $\Gamma_v = 5A_1 + 3A_2 + 3B_1 + 4B_2$, and all classes occur in the Raman spectrum (15 vibrations) but in the infrared class A_2 does not appear (12 vibrations). Their infrared results are incomplete so that the symmetry group cannot be deduced unequivocally.

They assign the infrared and Raman peak at 655 cm.$^{-1}$ to a S–O–S vibration. However, all the compounds used to support their arguments have S–O bonds. In the Raman spectra[14] of $S_2O_5^{2-}$ and the polythionates the 650 cm.$^{-1}$ frequency also occurs (see following Table). Hence Simon and Waldmann's assignment of the S–O–S vibration to the 650 cm.$^{-1}$ frequency is not correct for $S_2O_5^{2-}$. Consequently, their reaction mechanism for the formation of pyrosulphite is incorrect. It seems most unlikely that the $S_2O_5^{2-}$ ion would be formed from the $HO{\cdot}SO_2^-$ species only, since they showed that $H{-}SO_3^-$ existed mainly (detected H–S vibration) at large concentrations. Formation of the S–S bonded $S_2O_5^{2-}$ ion seems much more likely through the hydrogen-bonded bisulphite species (III). The following Table gives a summary of the species present in a pyrosulphite solution.

Substance	ν_3 (cm.$^{-1}$) (S–O)	Substance	ν_3 (cm.$^{-1}$) (S–O)	Substance	ν_3 (cm.$^{-1}$) (S–O)
$S{-}SO_3$	660	$O_3S{-}S_2{-}SO_3$ ...	660	$O_2S{-}SO_3$	650
$O_3S{-}S{-}SO_3$ ...	610	$O_3S{-}S_3{-}SO_3$ ...	650		

Species	$\lambda_{max.}$ (mμ)	log $\varepsilon_{max.}$	f
Bisulphite (I)	205·2	2·75 (apparent)	$4{\cdot}6 \times 10^{-3}$ (apparent)
Bisulphite (III)	215	1·85	$9{\cdot}2 \times 10^{-4}$
$S_2O_5^{2-}$	255	3·60	$8{\cdot}3 \times 10^{-3}$

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[*Received, December 1st,* 1959.]

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[11] Martin and Rossotti, *Proc. Chem. Soc.*, 1959, 60.
[12] Zachariasen, *Phys. Rev.*, 1932, **40**, 923.
[13] Lindquist and Mortsell, *Acta Cryst.*, 1957, **10**, 406.
[14] Eucken and Wagner, *Acta Phys. Austriaca*, 1948, **1**, 339.