

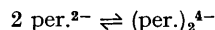
Dimerization of Periodate in Aqueous Solution, and the Second Dissociation Constant of Periodic Acid

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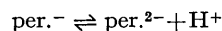
A dimeric periodate species is known in the solid state in potassium dimesoperiodate,¹ $K_4I_2O_9$, but no such species has been reported in aqueous solution. Crouthamel *et al.*² made an extensive study of the ultraviolet absorption spectra of aqueous periodate solutions, but their work was confined to periodate concentrations less than $3 \times 10^{-4}M$, and no deviations from Beer's law were found. The first indication of the existence of a dimeric species in solution came from a kinetic study³ of the pinacol-periodate reaction at 0° . In neutral and acid solution first-order kinetics with respect to each reactant were observed, as reported by other workers,⁴ but at pH 10 the order with respect to periodate decreased from 1.0 to 0.6 with increase of periodate concentration from 10^{-5} to $10^{-2}M$. First-order kinetics with respect to pinacol were still observed, irrespective of concentration. This result could only be interpreted by assuming that dimerization of the periodate occurred, and that the pinacol only reacted with a monomeric species. Accordingly, the ultraviolet absorption spectra of periodate solutions at pH 11.4 and 1.0° were investigated in the concentration range 10^{-5} to $10^{-2}M$. Short path length cells were used at the higher concentrations to keep the optical density below 1.2, and a constant ionic strength of 0.10 was maintained by the addition of

potassium chloride. A marked shift in the spectrum with increase of periodate concentration was observed; the peak at $210 m\mu$ characteristic of monomeric periodate²⁻ was shifted to longer wavelengths, and isosbestic points were found at 217.5, 251, and $276 m\mu$. Quantitatively the results were in accord with the following equilibrium:



The mean value of the equilibrium constant is $2400 \text{ mole l.}^{-1}$. The spectrum of the dimer consists of a broad band with $\lambda_{\text{max.}}$ $228 m\mu$ and $\log \epsilon_{\text{max.}}$ 4.22. A similar study at 25.0° gave a value of 660 mole l.^{-1} for the equilibrium constant at an ionic strength of 0.10. No dimerization of periodate⁻ (pH 5) could be detected; the spectrum of 0.1M-sodium metaperiodate was identical with that given by a $10^{-4}M$ -solution.

Further confirmation of dimer formation came from potentiometric titrations of periodic acid at various concentrations and temperatures. Values of the apparent second dissociation constant were calculated (see Table), *i.e.* the following equilibrium was assumed:



Corrections were made for activity coefficients. The pK_2 values are qualitatively in accord with

¹ A. E. Hill, *J. Amer. Chem. Soc.*, 1928, **50**, 2679.

² C. E. Crouthamel, A. M. Hayes, and D. S. Martin, *J. Amer. Chem. Soc.*, 1951, **73**, 82.

³ G. J. Buist, unpublished work.

⁴ C. C. Price and H. Kroll, *J. Amer. Chem. Soc.*, 1938, **60**, 2726; F. R. Duke and V. C. Bulgrin, *ibid.*, 1954, **76**, 3803.

the spectrophotometric results; increase in the degree of dimerization increases the acid strength. By making a correction for the amount of dimer

Apparent pK_2 values of periodic acid (concentrations in mole l^{-1})

0°		25°		45°	
[Per.]	pK_2	[Per.]	pK_2	[Per.]	pK_2
0.002	8.08	0.002	8.22	0.002	8.43
0.010	7.89	0.030	8.02	0.010	8.46
0.020	7.66	0.05	7.90	0.05	8.30

present in the 0.002M titrations, the true values of the second dissociation constant were calculated: $pK_2 = 8.34, 8.33,$ and 8.43 at $0^\circ, 25^\circ,$ and 45° respectively (no correction required at 45°). The value 7.40 reported by Crouthamel *et al.*² for 0° is evidently low, due to neglect of dimer formation.

The dimer is probably the dimesoperiodate ion $(O_4I-O-IO_4)^{4-}$. Hydrated forms such as $(H_2O_5I-O-IO_5H_2)^{4-}$ are less probable as the corresponding acids would be weak.

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