

CHAPTER - I I

EXPERIMENTAL TECHNIQUE

Peroxydisulphate has been used for the oxidation of many systems. Oxidation by peroxydisulphate ion generally takes place slowly, but become fairly rapid in the presence of a catalyst.

The reactions of $S_2O_8^{2-}$ are known to be greatly influenced by traces of impurities, hence all possible precautions were taken to avoid the impurities in the reaction system from reagents to reaction vessels.

Potassium peroxydisulphate of A.R.E.Merck quality was always used after recrystallisation from its saturated solution in conductivity water and drying at room temperature under vacuum. As the reaction rate is affected even by traces of impurities the solutions were always prepared in conductivity water. Potassium peroxydisulphate slowly decomposes not only in solution but also in solid state. Peroxydisulphate was always tested for sulphate ions and recrystallised again if sulphate ions appeared in the sample. The conductivity water was prepared by redistilling the distilled water in pyrex glass distilling still to which a few crystals of $KMnO_4$ and KOH added. The purity of conductivity water was always checked by conductivity measurements.

Standard solution of peroxydisulphate was always prepared by the exactly weighed quantity of the recrystallised peroxydisulphate in conductivity water using measuring flasks of pyrex glass. The aqueous solution of $S_2O_8^{2-}$ decomposes slightly on standing. Therefore a freshly prepared solution of peroxydisulphate was used. The strength of $S_2O_8^{2-}$ solution was always checked by arsenite¹⁷¹ method or iodometric method, described in detail later on in this chapter.

The catalyst, silver nitrate, used was of B.D.H. Analar quality. The standard solution of $AgNO_3$ was prepared by directly weighing the salt and dissolving it in requisite quantity of conductivity water. The solution was stored in a stoppered pyrex glass flask coated on outside with black Japan and further wrapped with black cloth to avoid photochemical effects.

B.D.H. or E.Merk quality of amides were used. The purity of the compound was checked by determining their melting points. Standard solutions were prepared by exactly weighing the calculated quantity of amide and dissolving it in conductivity water, in a standard pyrex glass measuring flask.

B.D.H. , Analar quality of starch indicator was prepared by dissolving approximately weighed soluble starch in boiling distilled water. A pinch of mercurous iodide was added for greater stability of starch solution.

All the reactions were carried out in glass stoppered vessels of pyrex glass or in iodine flasks. The flasks were coated on the outside with black Japan and wrapped in black cloth, to avoid any possibility of photochemical effect.

Calculated amounts of the reactants were kept separately in a thermostatic water bath (accuracy $\pm 0.1^\circ\text{C}$) maintained at the desired temperature of the experiment. Solutions were kept for 15 minutes in order to attain the temperature of the bath.

The three solutions were rapidly mixed and aliquot of the reaction mixture was withdrawn at suitable intervals of time. This aliquot was added to a mixture of KI, FeSO_4 and CuSO_4 (KI \longrightarrow 10% \longrightarrow 10 ml, FeSO_4 \longrightarrow 1% \longrightarrow 1 ml and CuSO_4 \longrightarrow 1% \longrightarrow 1 ml) in iodine flask. The iodine flask was stoppered and allowed to stand for about ten minutes for complete liberation of iodine and the equivalent iodine liberated was titrated against a standardised sodium thiosulphate using starch as an indicator.

Various iodometric methods for estimating unreacted peroxydisulphate^{14, 171} were suggested from time to time, but in this kinetic study the method of Szabo¹⁸³ Csayni and Galiba (as further modified by Khulbe⁷⁰ and Srivastava) as given above was used for kinetic study.

The blank titrations were carried out by taking 10 ml of 10% KI, 1 ml of 1% CuSO_4 and 1 ml ^{of 1%.} FeSO_4 , in order to

evaluate the quantity of sodium thiosulphate, corresponding to the iodine liberated by CuSO_4 and FeSO_4 mixture alone. The volume of sodium thiosulphate equivalent to unreacted peroxydisulphate was determined by subtracting the titre value of blank titration from the titre value for the reaction mixture.

The amides used did not interfere with this method of estimation of peroxydisulphate. Throughout the kinetic study, a simultaneous study of the silver catalysed self decomposition of peroxydisulphate alone, under exactly similar conditions has been carried out in each case.

In recording the observations for different kinetic runs, the following observations are used.

1. 'C' denotes the volume in ml of the standard $\text{Na}_2\text{S}_2\text{O}_3$ solution equivalent to the unreacted $\text{K}_2\text{S}_2\text{O}_8$ at any time interval.
2. ' k_1 ' represents the first order rate constant for the total reaction.
3. ' k_2 ' represents the first order rate constant for the Ag^+ catalysed self decomposition of $\text{S}_2\text{O}_8^{2-}$ under exactly similar experimental condition as for the determination of k_1 .
4. 'k' denotes the rate constant for the oxidation of substrate alone. It has been evaluated by subtracting k_2 from k_1 . Thus the net $k = (k_1 - k_2)$.
5. 'min' denotes minutes and 'conc' denotes the concentration.

The data for different kinetic runs for self decomposition although carried out in each case, has not been given for all cases. Only for the first compound, the self decomposition of peroxydisulphate has^{been} shown. Similarly for the other compound, the self decomposition was carried out and only k_2 values are given at the end of each table.

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