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Optimum Conditions for Hydrogen Peroxide Oxidation of Thiocyanate to Sulphate

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Ammonium or potassium thiocyanate is oxidised quantitatively (yield 97-99%) to sulphate by 30% H_2O_2 at *p*H 7-8 and SCN^- : H_2O_2 molar ratio of 1:8-10.

It is known that hydrogen peroxide oxidation of thiocyanate in solution to yield sulphate is an electron transfer reaction[1] but the optimum conditions like *p*H, molar ratio between SCN^- and H_2O_2 etc. required for the quantitative oxidation do not appear to have been reported so far. The optimum conditions for the quantitative conversion of SCN^- into SO_4^{2-} in the above reaction have now been worked out and are reported in this note.

All the chemicals used were of reagent grade quality.

Procedure for quantitative conversion of SCN^- into SO_4^{2-}

Ammonium or potassium thiocyanate (1 mol) was dissolved in 30% (v/v) H_2O_2 (8-10 mol) and filtered. To the filtrate was added the corresponding alkali hydroxide in portions, with constant stirring, until the *p*H of the solution was raised to 7-8. The solution was stirred for about 10 min and excess of ethanol added until the white crystalline sulphate ceased to appear. The compound was filtered, washed 3-4 times with ethanol, and dried *in vacuo* over phosphorous pentoxide.

The oxidation of NH_4SCN (2 g; 26.3 mmol) with 30% H_2O_2 (27 ml; 237.6 mmol) gave $(NH_4)_2SO_4$ in quantitative yield (3.44 g; 99%), while the reaction of KSCN (2 g; 20.6 mmol) with 30% H_2O_2 (23.4 ml; 206 mmol) gave K_2SO_4 in quantitative yield (3.52 g; 98%).

The thiocyanate oxidation reaction was monitored by IR spectroscopy. The complete disappearance of $\nu(C\equiv N)$ and $\nu(C-S)$ (ref. 2) around 2050 and 750 cm^{-1} respectively, and appearance of two sharp bands at 1110 and 610 cm^{-1} due to ν_3 and ν_4 modes respectively[3] of SO_4^{2-}, in a small amount of the sample isolated from the reaction solution, ensured completion of the reaction.

Sulphate was determined gravimetrically as barium sulphate. potassium and nitrogen were estimated by the methods described earlier[4]. The analytical results agreed very well with the values calculated for the corresponding sulphates. The purity of the compounds was checked by measuring their molar conductances (240-250 ohm^{-1} cm^2 mol^{-1}).

It was found that the oxidation of NH_4/K thiocyanates to sulphates was quantitative (sulphate yield 97-99%) in the *p*H range 7-8. The most suitable ratio of SCN^- : H_2O_2, for quantitative oxidation, was found to be 1:8-10, although stoichiometrically one mol of SCN^- would require 3 mol of H_2O_2. A molar ratio of 1: ≤ 6 (SCN^-:H_2O_2) did not give the sulphates in quantitative yields owing to the possibility of sulphur being present as $S(CN)_2$ under this condition[1]. A higher ratio of SCN^-:H_2O_2 (1: > 10) was not considered desirable for two reasons: (i) at high ratios H_2O_2 decomposes to give oxygen[1], and (ii) there is a possibility of contamination of sulphate by ammonia and nitrate, which are formed under this condition[1].

Since SCN^- is the conjugate base of a weak acid, it exists largely as SCN^- under neutral conditions (*p*H 7-8). Moreover, H_2O_2 behaves as a poor oxidant at lower *p*H; thus a low yield of sulphate at *p*H < 7 is not unexpected. At *p*H > 8, the alkali-induced decomposition[5] of H_2O_2 and the slow reaction between HOCN (another oxidation product of SCN^-) and H_2O (ref. 1) are responsible for lowering the yield of the sulphate.

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