Specific Effects of Electrolytes on the Oxidation of Sulphite by Hexacyanoferrate(III)

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IN an investigation of the effect of ionic strength on the course of the reaction

$$2[Fe(CN)_6]^{3-} + SO_3^{2-} + 2\,OH^- \rightarrow SO_4^{2-} + [Fe(CN)_6]^{4-} + H_2O$$

Swinehart[1] found that identical concentrations of the "inert" ions Na^+, K^+, and NMe_4^+, have differing effects in addition to the unusual effects of inert electrolytes previously observed.[2] The established specific effects of "inert" cations were explained by Swinehart[1] on the assumption that the cation may act either as an actual bridge for electron transfer or as a means of allowing the two negatively charged ions to approach close enough for electron transfer through the solvent. The specific influences of "inert" ions on other oxidation–reduction reactions (*e.g.* MnO_4^-–MnO_4^{2-}; $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$; $S_2O_8^{2-}$–I^-) were interpreted by a similar mechanism.[3]

We have re-investigated the influence of the ionic strength on the oxidation of sulphite by hexacyanoferrate(III), and have found that the reaction is influenced both by cations and anions (Figure 1).

As no satisfactory explanation of these effects was found, a specific effect of trace impurities was sought. We found that the rate of the oxidation of sulphite by hexacyanoferrate(III) is appreciably enhanced by cupric ions in trace concentration (Figure 2). Other ions, in the same concentration, do not influence the reaction velocity significantly.

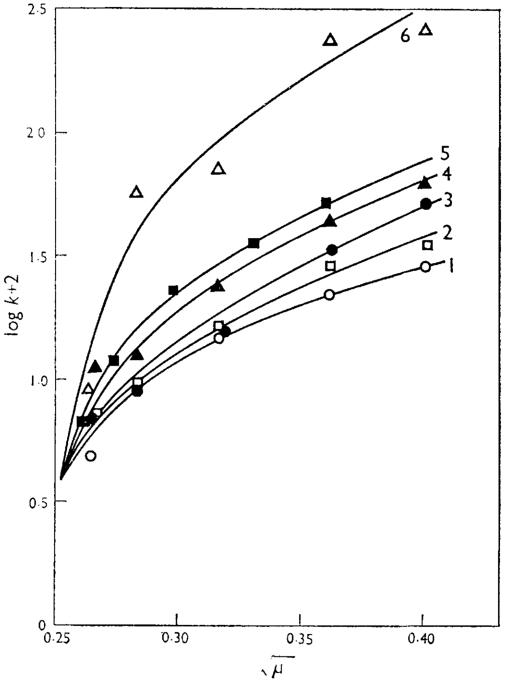

FIGURE 1.

The effect of "inert" electrolytes on the oxidation of sulphite by hexacyanoferrate(III).
$[Fe(CN)_6^{3-}]_{t=0} = 10^{-3}$ M; $[SO_3^{2-}]_{t=0} = 1.85 \times 10^{-2}$ M; N_2 atmosphere; 25°; μ = ionic strength; k = second order rate constant [l.mole^{-1} sec.$^{-1}$];
1 NaCl, 2 NaF, 3 KCl, 4 KBr, 5 KF, 6 NaBr.

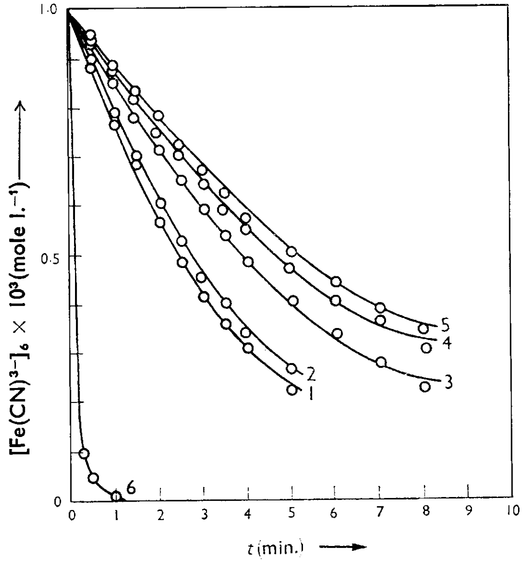

FIGURE 2.

The influence of $CuCl_2$ *and* Na_2EDTA *on the reaction velocity.*
$[Fe(CN)_6^{3-}]_{t=0} = 10^{-3}$ M; $[SO_3^{2-}]_{t=0} = 3.64 \times 10^{-2}$ M; Britton–Robinson buffer, pH 10.5; N_2 atmosphere; 25°. Curves 1—5: 0: 1×10^{-5}, 4×10^{-5}, 6×10^{-4}, 4×10^{-3} M-Na_2EDTA and 6: 10^{-5} M-$CuCl_2$.

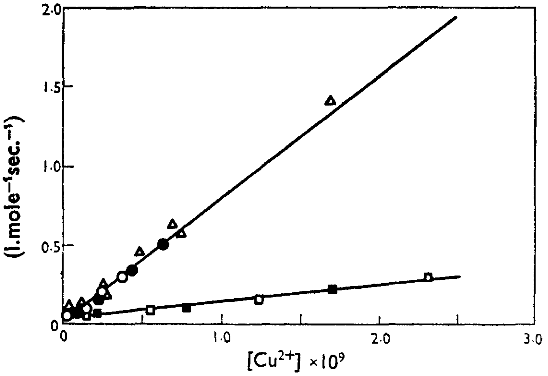

FIGURE 3.

Plot of velocity constants found in different electrolyte solutions against [Cu^{2+}].

$[Fe(CN)_6^{3-}]_{t=0} = 10^{-3}$ M; $[SO_3^{2-}]_{t=0} = 1{\cdot}85 \times 10^{-2}$M

N_2 atmosphere; 25°.

○ = NaCl; ● = KCl; △ = NaBr; ▲ = KBr;

□ = NaF; ■ = KF.

In order to prove that the specific effects of "inert" electrolytes on the oxidation of sulphite by hexacyanoferrate(III) are in fact caused by different amounts of cupric ion present as an impurity, we have plotted the velocity constants, found for different salts at different concentrations, against the concentration of cupric ions. The concentration of cupric ion has been determined analytically by means of the atomic absorption (Figure 3): the velocity constants are proportional to this concentration. The different slope found in the solutions of fluorides is probably caused by the different complexing ability of the fluoride ion.

It seems possible that some further so-called "specific effects of inert ions",[4] are caused by the catalytical influence of the trace impurities.

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