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OXIDATIONS BY MANGANESE(III)—II. OXIDATION OF CHROMIUM(III)

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Abstract—The oxidation of chromium(III) by manganese(III) in sulphuric acid solution was followed by extracting aliquots of the quenched reaction mixture with a dibutyl phosphate–xylene solution. The absorbance of the manganese(III) dibutyl phosphate complex gave the concentration of manganese(III) as the reaction proceeded. The reaction followed second-order kinetics. Applying the Eyring equation to the rate constants at different temperatures, gave an activation enthalpy of 129 kJ mol^{-1} and entropy of 140 J K^{-1} mol^{-1}. The suggested mechanism includes a bimolecular slow oxidation of chromium(III) to chromium(IV) by manganese(III), followed by faster oxidations of chromium(IV) and chromium(V) by manganese(III), which is reduced in each stage to manganese(II). Spectral examination proved that $Cr_2O_7^{2-}$ ions are ultimately produced.

Qualitatively, the oxidation of acidified chromium(III) solutions to dichromate by manganese(III) has been reported earlier. An investigation of the oxidation of chromium(III) by various manganese oxides indicated that manganese(III) ions from the solid oxides may be responsible for the oxidation. Later, kinetic studies of the reaction between manganese(III) and chromium(III) showed that it followed second-order kinetics. However, the spectrophotometric technique used encountered a problem of overlapping of the spectra of the reactants and products. A suggested procedure for the separation of manganese(III), based on its extraction with dibutyl phosphate solution, has been developed in the present investigation. The coloured compound extracted was found to be the dibutyl phosphate of manganese(III).

EXPERIMENTAL

Manganese(III) sulphate solutions were freshly prepared by the oxidation of manganese(II) sulphate, in sulphuric acid, by potassium permanganate solutions. The resulting solution was standardized against standard iron(II) or ascorbic acid solution, prepared using boiled-out distilled water. Measured volumes of A.R. chrome alum solution in sulphuric acid were heated in the flash of a reaction vessel at a temperature above that planned for the kinetic run, and then thoroughly mixed with the manganese(III) solution kept at room temperature. A constant ionic strength was maintained by adding sodium sulphate to the reaction mixture. The reaction mixture was placed in a thermostat and aliquots were withdrawn at intervals into bulbs cooled in salt and ice. A quenched aliquot was extracted with an equal volume of Fluka dibutyl phosphate in A.R. xylene (1 : 5 by volume). The absorbance of the organic layer, dried with anhydrous sodium sulphate, was measured at the maximum wavelength of absorption (537 nm). Beer's law was found to be applicable to the coloured solutions. This was established by extracting standardized manganese(III) solutions and measuring the absorbance of the organic layer at the above wavelength.

RESULTS AND DISCUSSION

Figure 1 depicts the results of duplicate runs in which equal concentrations of reactants were mixed at four different temperatures. The reciprocal of the manganese(III) concentration is plotted against time. The rate constants, k_r, calculated from the plots, were used to calculate the activation enthalpy $\Delta H^\ddagger$ and entropy $\Delta S^\ddagger$ using the Eyring equation:

$$\ln(k_r h/KT) = \Delta H^\ddagger/RT + \Delta S^\ddagger/R.$$

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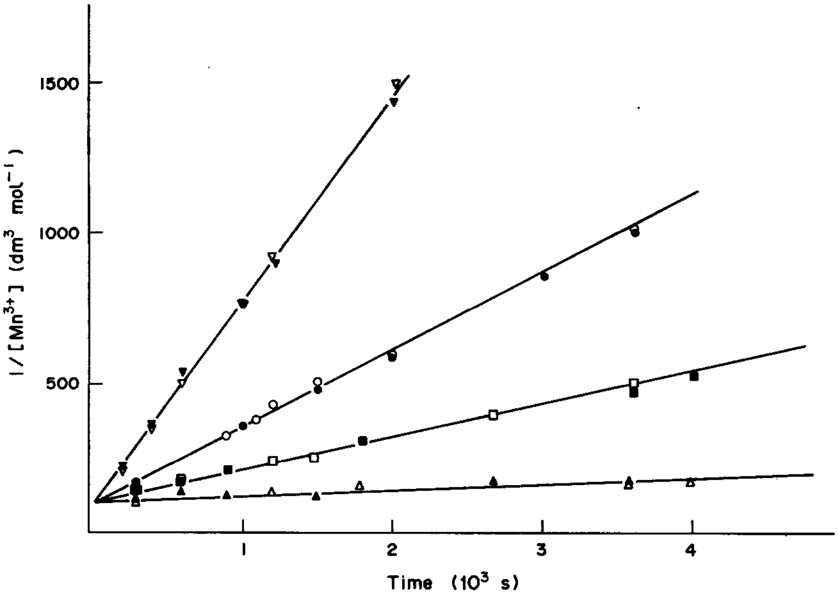

Fig. 1. Variation of the reciprocal of the concentration of manganese(III) with the reaction time at 36°C (△, ▲), 44°C (□, ■), 50°C (○, ●) and 58°C (▽, ▼).

The activation enthalpy estimated from the slope of the plot in Fig. 2 was 129 kJ mol^{-1} and the activation entropy was 140 J K^{-1} mol^{-1}. The mechanism suggested is:

$$Cr^{3+} + Mn^{3+} \xrightarrow{k_1} Cr^{IV} + Mn^{2+}$$

$$Cr^{IV} + Mn^{3+} \xrightarrow{k_2} Cr^{V} + Mn^{2+}$$

$$Cr^{V} + Mn^{3+} \xrightarrow{k_3} Cr^{IV} + Mn^{2+}.$$

If $k_1 \ll k_2$ and k_3, the bimolecular reaction becomes rate-determining. Both chromium(IV) and chromium(V) have been postulated in the reactions involving oxidations by dichromate. The latter ions were identified in the spectra of reaction mixtures near the end of the reaction.

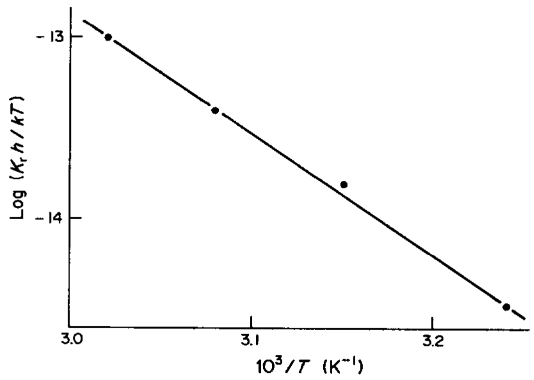

Fig. 2. Variation of $\log(k_r h/kT)$ with the reciprocal of the thermodynamic temperature.