

Studies of the Reactions between the Chromium(VI) Ion
and some Biological Reductants

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The kinetics of the reduction of 'free' and coordinated chromium(VI) ion by L-ascorbic acid, DL-penicillamine, glutathione and L-cysteine have been studied under varying conditions.

The reduction of the 'free' chromium(VI) ion by L-ascorbic acid proceeds through the rate determining formation of a chromate-ascorbate intermediate. The rate constant k_f for its formation, ranges from $50.9 \pm 0.9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to $0.56 \pm 0.02 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the pH range 4.60-7.40. The subsequent decomposition of this chromium(VI) intermediate occurs through a series of rapid one electron transfers leading ultimately to the formation of chromium(III). The reduction of chromium(VI) by DL-penicillamine at neutral pH is a second order process, with $k = 0.23 \pm 0.00 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C.

Unlike the other reductants, second order ligand dependencies were observed in the glutathione

reactions. The third order rate constant at 25°C was determined as $1.97 \pm 0.07 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

The rate constants are dependent on pH for the ascorbate reaction and the three forms of ascorbate present in aqueous solution reduce chromate in the order $\text{H}_2\text{A} > \text{HA}^- \gg \text{A}^{2-}$, while a protonated sulphhydryl group of the thiols seems to be quite reactive.

This trend is also true for the reactions of these three reductants as well as L-cysteine, with a coordinated chromium complex, pentaamminechromato-cobalt(III) nitrate, $[(\text{NH}_3)_5\text{CoOCrO}_3]\text{NO}_3$.

These reactions are typically biphasic in nature and proceed with an initial rapid increase in absorbance followed by a slower gradual decrease. The initial phase involves precursor complex formation between the chromato complex and 1 mole each of L-ascorbic acid, L-cysteine and DL-penicillamine respectively. The activation parameters for these reactions are fairly similar: $\Delta\text{H}^\ddagger = 20.4 \pm 16 \text{ kJ mol}^{-1}$, $\Delta\text{S}^\ddagger = -204 \pm 16 \text{ J mol}^{-1} \text{ K}^{-1}$; $\Delta\text{H}^\ddagger = 23.6 \pm 6.8 \text{ kJ mol}^{-1}$, $\Delta\text{S}^\ddagger = -210 \pm 28 \text{ J mol}^{-1} \text{ K}^{-1}$; $\Delta\text{H}^\ddagger = 31.5 \pm 3.2 \text{ kJ mol}^{-1}$, $\Delta\text{S}^\ddagger = -188.7 \pm 12.7 \text{ J mol}^{-1} \text{ K}^{-1}$; (for the three reductants in the order listed above), indicating that a similar mechanism might be operative.

Based on kinetic results, it seems that two moles

of glutathione are required for the initial reaction with the chromato complex. Substantial proof comes from fitting the kinetic data to a nonlinear expression of the form: $k = a[\text{GSH}]^n$. The value of 'n' at 25.3°C is 1.87 ± 0.09 . Its corresponding thermodynamic parameters are: $\Delta H^\ddagger = 16 \pm 2.3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -16.3 \pm 9.7 \text{ J mol}^{-1} \text{ K}^{-1}$, and is a reflection of the disparity in mechanism compared to the other reductants.

Kinetic and thermodynamic information on the second stage of the reaction between the chromato complex and the four reductants prove that this step incorporates the reduction of the chromium in the complex, and this may be very similar to the reduction of the free ion.

Despite this apparent similarity, the second metal ion, cobalt(III), can complicate the overall kinetics, as it is reduced by L-ascorbic acid and forms a series of brown complexes with the thiols.

The absence of dissolved oxygen from kinetic solutions containing L-ascorbic acid and L-cysteine as the reductants, results in a dramatic increase in the k_{obs} values. A dead-end type mechanism is proposed to explain this trend.