ABSTRACT

KINETICS AND MECHANISMS OF THE REACTIONS OF CHROMIUM(VI) WITH SULFUR-CONTAINING COMPOUNDS IN AQUEOUS ACID SOLUTION

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The kinetics of the reactions of chromium(VI) with sulfur(IV), thioglycolic acid, 2-mercaptosuccinic acid, *meso*-2,3-dimercaptosuccinic acid, and 2-mercaptoethanesulfonic acid were studied spectrophotometrically.

Sulfur(IV) reacts with chromium(VI) by the rapid equilibrium formation of an O-bonded intermediate which was not spectrally defined. Subsequent decay of this intermediate produced a S-bonded chromium(III) product which fitted a mixed order rate expression. The kinetic parameters are $K_1' = (1.82 \pm 0.09) \times 10^4\ M^{-1}$, $k_1 = (9.97 \pm 0.08) \times 10^4\ M^{-1}s^{-1}$, $k_2 = 54 \pm 2\ M^{-1}s^{-1}$ at 25.0 °C.

The reaction of chromium(VI) with thioglycolic acid proceeds by the rapid formation of an O-bonded thioglycolato chromium(VI) complex which was spectrally undefined. This complex is then transformed to the corresponding S-bonded chromium(VI) thioester which has λ_{max} at 425 nm.

The kinetic parameters obtained are k_{F2} = 29.5 ± 0.4 $M^{-1}s^{-1}$, k_{F3} = 2.3 ± 0.2 $M^{-1}s^{-1}$ and the equilibrium constant is (8 ± 5) x 10^{-3} M^{-1} at 25.0 °C. The nature and concentration of the buffer medium was found to affect the formation process. This S-bonded species undergoes bimolecular electron transfer with specific rate constants k_{D2} = 11.5 ± 0.3 $M^{-1}s^{-1}$, k_{D3} = 2.0 ± 0.4 $M^{-1}s^{-1}$ at 25.0 °C. The activation parameters of the formation and decay processes are similar.

The reaction of chromium(VI) with 2-mercaptosuccinic acid proceeds similarly to that of thioglycolic acid. The recorded second-order rate and equilibrium constants for the formation process are k_{F2} = 109 ± 2 $M^{-1}s^{-1}$, k_{F3} = 17.2 ± 0.7 $M^{-1}s^{-1}$, K_{MSOH} = (12 ± 2) x 10^{-3} M^{-1} at 25.0 °C. The second-order rate constants for the decay of the chromium(VI) thioester intermediate are k_{D1} = 18.7 ± 0.2 $M^{-1}s^{-1}$, k_{D2} = 5.3 ± 0.1 $M^{-1}s^{-1}$, and k_{D3} = 0.2 ± 0.1 $M^{-1}s^{-1}$ at 25.0 °C.

Similar reactions occur in the formation of the intermediate between chromium(VI) and *meso*-2,3-dimercaptosuccinic acid. The second-order rate constants for the formation of the chromium(VI) thioester intermediate with *meso*-2,3-dimercaptosuccinic acid are k_{F1} = 740 ± 40 $M^{-1}s^{-1}$, k_{F2} = 180 ± 6 $M^{-1}s^{-1}$ at 25.0 °C. The reduction of the chromium(VI) *meso*-2,3-dimercaptosuccinic acid intermediate was different in that it goes via the formation of an adduct followed by a uni-molecular electron transfer. Only

composite rate constants of the order $k_{D2}K_{D1}$ = 112 ± 2 $M^{-1}s^{-1}$ at 25.0 °C, were deduced.

The reaction of chromium(VI) with 2-mercaptoethanesulfonic acid showed the direct formation of a S-bonded chromium(VI) thioester with no evidence of any O-bonded species. The kinetics were explained by the simple acid-base behaviour of chromium(VI) and 2-mercaptoethanesulfonic acid. These rates were significantly slower than the other systems. The second-order rate constants for the formation of the intermediate are k_{F1} = 45.2 ± 0.7 $M^{-1}s^{-1}$, k_{F3} = 0.64 ± 0.08 $M^{-1}s^{-1}$ at 24.8 °C. The corresponding second-order rate constants for the decay processes are k_{D1} = 2.58 ± 0.07 $M^{-1}s^{-1}$, k_{D2} = (8.8 ± 0.3) x 10^{-2} $M^{-1}s^{-1}$, and the equilibrium constant K_{TE} = (1.2 ± 0.4) x 10^{-7} M^{-1} at 24.8 °C.

In all the cases, the O-bonded species were spectrally undetected and highly labile. The lack of a carboxylate group in 2-mercaptoethanesulfonic acid produced a significantly different kinetic behaviour.

The substitution reactions were faster than the electron transfer processes. All the reactions were highly entropy driven with large negative values, indicating the associative nature of the various reactions.