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Kinetic control of the aquation of the hexathiocyanatochromate(III) ion by associative interaction of poly(acrylamide) in aqueous medium

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Cooperative interaction of poly(acrylamide) is found to decelerate significantly the aquation rate of $[Cr(NCS)_6]^{3-}$ in acidic, neutral, and basic media, which is an indication of kinetic control of macromolecules on reactions.

Keywords: chromium(III) complex, macromolecular effect on rate

A recent preliminary communication[1] on macromolecular influence in the aquation mechanisms of chromium(III) complexes has established several features of kinetic interest. The substitution reactions of $[Cr(NCS)_6]^{3-}$ have been the subject of many discussions in which the acid-catalysed reactions of this complex are reasonably well understood and in basic solutions enhanced ligand replacement was observed. More mechanistic informations on the reaction rate can be obtained by investigating the kinetics in heterogeneous media.[1] Zinato *et al.*[4] established that $[Cr(CN)_6]^{3-}$ undergoes reduced rate in a medium containing a polyaza-macrocyclic ligand. It appears to be more interesting to study the aquation of $[Cr(NCS)_6]^{3-}$ in the presence of an inert polymer like poly(acrylamide) PAA, to obtain additional information on the reaction mechanisms as well as on the interaction behaviour between complex and macromolecule. In the present investigation the aquation of $[Cr(NCS)_6]^{3-}$ was carried out in a medium containing 0.5% poly(acrylamide), PAA. The rate has been investigated as a function of the molecular weight of added PAA and at three temperatures in acidic, neutral and basic media (molecular weight of poly(acrylamide) 42000, 83000, 121000, 232000 and 447000, temperatures 315, 323 and 333K).

Ionic strength of the medium was kept at 0.01M ClO_4^- using $NaClO_4$ in acidic and basic solutions but 0.1M in neutral solutions. Similar studies were repeated in presence of 0.5% PAA of varying molecular weight at pH 1 acidic (0.1M $HClO_4$) pH 7, neutral (0.1M $NaClO_4$) and pH 12 basic (0.01M NaOH) solutions. The reaction was followed spectrophotometrically by monitoring the decrease in absorbance at 563 nm where the complex shows maximum absorption. Pseudo first order rate constants k_{obs}, were obtained from a linear least squares fit of the first order plot of log $(A_t – A_i)$ *vs* time, where A_t and A_i are the absorbances at time '*t*' and infinite time respectively. Runs were followed from 4 to 8 half-lives. The standard deviations for k_{obs} were always less than 1%; values for k_{obs} in duplicate runs were within 5% of each other.

All the $[Cr(NCS)_6]^{3-}$ solutions containing up to 0.5% PAA cause no change in the initial electronic absorption spectrum of the complex. The rate of aquation of $[Cr(NCS)_6]^{3-}$ in acidic and neutral solutions containing 0.5% PAA is slow, while in basic solution the complex undergoes fast NCS^- replacement. Aquation is accompanied by a spectral shift of the ligand field maxima, consistent with coordination of the spectrochemically weaker H_2O ligand. The general reaction sequences[7] are represented by the following reaction scheme.

Acidic solution

$$[Cr(NCS)_6]^{3-} + H_3O^+ \rightarrow \{Cr(NCS)_6(H_2O)^{3-}\} + H^+ \quad (1)$$

$$\{Cr(NCS)_6(H_2O)^{3-}\} \rightarrow [Cr(NCS)_5(H_2O)]^{2-} + NCS^- \quad (2)$$

Neutral solution

$$[Cr(NCS)_6]^{3-} + H_2O \rightarrow \{Cr(NCS)_6(H_2O)^{3-}\} \quad (3)$$

$$\{Cr(NCS)_6(H_2O)^{3-}\} \rightarrow [Cr(NCS)_5(H_2O)]^{2-} + NCS^- \quad (4)$$

$$\{Cr(NCS)_6(H_2O)^{3-}\} \rightarrow [Cr(NCS)_5(OH)]^{3-} + NCS^- + H^+ \quad (5)$$

Basic solution

$$[Cr(NCS)_6]^{3-} + OH^- \rightarrow \{Cr(NCS)_6(OH)^{4-}\} \quad (6)$$

$$\{Cr(NCS)_6(OH)^{4-}\} \rightarrow [Cr(NCS)_5(OH)]^{3-} + OH^- \quad (7)$$

Scheme 1

Table 4 Extrapolated rate constant (k_o) and association constant (k_p) for the aquation of $Cr(NCS)_6^{3-}$ in 0.5% poly(acrylamide) solutions

	Temperatures (K)		
Constant	315	323	333
Acidic solution (pH = 1)			
10^5 k_o, s^{-1}	5.96±0.02	8.89±0.04	2.83±0.03
10^2 k_p, M^{-1} s^{-1}	1.72±0.06	3.63±0.07	4.59±0.08
r	0.927	0.933	0.846
Neutral solution (pH = 7)			
10^4 k_o, s^{-1}	1.01±0.04	1.92±0.06	3.63±0.07
10^2 k_p, M^{-1} s^{-1}	3.05±0.03	6.13±0.04	11.23±0.08
r	0.919	0.902	0.796
Basic solution (pH =12)			
10^4 k_o, s^{-1}	2.73±0.02	4.81±0.03	12.09±0.06
10^2 k_p, M^{-1} s^{-1}	6.51±0.02	15.54±0.05	43.77±0.05
r	0.928	0.864	0.805

k_o and k_p were evaluated from the linear regression analysis of $k_{obs} = k_o + k_p\ DP^{-1}$ where k_o (extrapolated rate constant) is the intercept term, k_p (association constant) is the positive slope value and *r* is the correlation coefficient.

The results of reactions carried out by keeping the concentration of $[Cr(NCS)_6]^{3-}$ fixed at 15 X 10^{-3}M and varying the degree of polymerisation of poly(acrylamide) added to the experimental solutions showed a linear decrease of reaction rate with increase in degree of polymerisation, DP, of PAA. This was determined by least squares analysis of data using Equation $k_{obs} = k_o + k_p\ DP^{-1}$, where k_o and k_p are the extrapolated and association constants obtained from linear least squares treatment of data, and are collected in Table 4. Arrhenius plots were used to calculate activation parameters.

The nature of the $[Cr(NCS)_6]^{3}$-poly(acrylamide) interaction is central to interpretation of our results. The rate constant, k_{obs}, in five water–PAA media is slower by *ca* 2.6 to 6.8 times than that measured in neat water at three different temperatures.[8] Moreover, there is a gradual reduction of rate constant ranging *ca* 1.3 to 1.9 times on passing from solutions containing low molecular weight PAA (42000) to high molecular weight PAA (447000). The degree of polymerisation or the molecular weight is taken to be an index of the total or cooperative effect of the macromolecule. Further, the cooperative effect of the polymer comprises three main effects: one is a steric effect, the second is a hydrophobic effect and the third is the electrostatic effect. Table 4 illustrates that in acidic medium, the functional groups of PAA are essentially protonated,

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such protonated polymer provides[12,13] steric, hydrophobic, and electrostatic effects for the complex ion. The net is the cooperative effect of PAA, characterised by the k_p values obtained from the linear equation. This is due to a consequence of $[Cr(NCS)_6]^3$-PAA adduct formation leading to decreased rate. On going from acidic to netural solution, the electrolyte present in the medium neutralises the charge of PAA and the electrostatic interaction between Cr(III) and PAA is reduced and the cooperative effect of PAA on $[Cr(NCS)_6]^{3-}$ is mainly due to steric and hydrophobic effects, which enables facile nucleophilic attack by both H_2O and OH^- at the Cr(III) centre results in increased rate.

The rate constants for base hydrolysis of $[Cr(NCS)_6]^{3-}$ are influenced by the macromolecule to a smaller extent than in acidic/neutral solutions, with increasing pH, steric, hydrophobic, electrostatic, and mobility of the PAA changes. This results in less negative $\Delta S^\#$ values in basic solutions, indicating that the transition state is less structured under such conditions. The weak PAA, when exposed to basic medium, results in increased conformational transition from a compact state to an expanded one as a consequence the steric, hydrophobic and electrostatic effect on Cr(III) decreases compared with the other two media. Considering rates of reactions, it is clear that the cooperative effect of PAA on $[Cr(NCS)_6]^{3-}$ shows selectivity more in acidic, moderate in neutral and low in basic media. The kinetically singnificant replacement of NCS^- occurs cooperatively within the macromolecular domain. Thus, a macromolecule added to a reaction system can bring considerable kinetic control by associative interaction with reactant/transition state owing to its specific cooperative effects.

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