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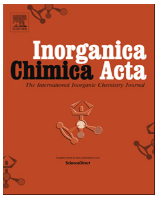

Equilibria and kinetics of chromium(VI) speciation in aqueous solution – A comprehensive study from pH 2 to 11

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ABSTRACT

A coherent and comprehensive speciation study was conducted in the aqueous Cr(VI) system in order to clarify several discrepancies in the literature. Using pH potentiometric UV–vis titrations and stopped-flow kinetic measurements, it was shown that the dominant Cr(VI) species are $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} in an aqueous solution of Cr(VI) under ambient conditions ([Cr(VI)] = 7.7 mM–155 mM, pH = 2–11, I = 1.00 M $NaClO_4$, T = 25.0 °C). This paper provides a comprehensive interpretation of the kinetic features of the dimerization equilibria of Cr(VI) in the acidic – alkaline pH range from pH 2 to 11. Under acidic conditions, the conversion of $HCrO_4^-$ and $Cr_2O_7^{2-}$ is catalyzed by H^+. This observation is consistent with the formation of a protonated intermediate, which is presumably $HCr_2O_7^-$. The forward and backward rate constants for the 2 $HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ reaction were determined at various pH values in concentration jump experiments. In the absence of catalysts, the slowest dimerization reaction was observed at pH 7 with a lifetime of a few minutes. At basic pH, OH^- reacts with $Cr_2O_7^{2-}$ to give CrO_4^{2-} on stopped-flow timescale. The basic hydrolysis of $Cr_2O_7^{2-}$ is irreversible, and the reaction is first order with respect to both $Cr_2O_7^{2-}$ and OH^-. The results presented here are consistent with some of the previously published experimental observations, and resolve the inconsistencies in the literature of Cr(VI) speciation.

1. Introduction

Chromium(VI) is one of the most widely studied high valent metal-oxo anions, partly owing to its toxicity. Because of its popularity, a lot of research groups characterized its aqueous speciation both from the thermodynamic and from the kinetic points of view. The numerous different approaches often led to apparent or real discrepancies, which are not resolved even in the modern literature. The current state of the Cr(VI) speciation literature is as follows.

Chemistry textbooks often discuss the presence of only CrO_4^{2-} – $Cr_2O_7^{2-}$ in an aqueous Cr(VI) solution. However, the existence of additional species has also been confirmed: hydrogen chromate or bichromate ($HCrO_4^-$), chromic acid (H_2CrO_4), hydrogen dichromate ($HCr_2O_7^-$), trichromate ($Cr_3O_{10}^{2-}$), and tetrachromate ($Cr_4O_{13}^{2-}$). While H_2CrO_4, $HCr_2O_7^-$, $Cr_3O_{10}^{2-}$ or $Cr_4O_{13}^{2-}$ only form under extreme conditions, at high acidity and very large Cr(VI) total concentration, [1] the mole fraction of the monomeric hydrogen chromate ion ($HCrO_4^-$) is significant even under pH 6.0. [2,3] It was stated that the UV–visible spectra of $HCrO_4^-$ and $Cr_2O_7^{2-}$ are essentially identical [4] or $HCrO_4^-$ is spectrophotometrically undetectable. [5] Cruywagen et. al. gave a detailed discussion concluding that there is no reason to doubt the existence of $HCrO_4^-$ from a theoretical point of view and also provided UV–vis spectroscopic evidence of hydrogen chromate. [6]

The kinetics of the hydrolysis of $Cr_2O_7^{2-}$ into CrO_4^{2-} was studied in the 1960's [7,8] and found to be catalyzed by both bases [9] and by acids. [10] Later, Brasch et. al. gave a critical summary about previous studies [11] which showed discrepancies both in the observed rates and in experimental rate laws. They concluded that this may in part be due to the inadequate methods of analysis including precipitation techniques, [12] mass spectrometry [13,14] and ^{17}O-NMR line broadening analysis. [15] Brasch et. al. also used ^{17}O-NMR to study the interconversion of the Cr(VI) species into each other and found that dimerization and hydrolytic reactions are catalyzed by nucleophiles, i.e. some of the applied buffers. However, their work was carried out in a limited pH range and did not confirm all of the earlier reports on the [H^+] and [OH^-] dependencies of the kinetics.

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As a summary, it is clear that there are still discrepancies in the literature regarding the speciation of Cr(VI). This, and the lack of a comprehensive study gave us the incentive to report a detailed thermodynamic and kinetic investigation of the protolytic and hydrolytic equilibria in an aqueous Cr(VI) solution. Moderate concentrations (1–155 mM) of Cr(VI) were used in order to provide coherent data for the broadest spectrum of applications.

2. Experimental

2.1. Chemicals and solutions

All chemicals were of analytical reagent grade, purchased from commercial sources and used as received without further purification. Aqueous Cr(VI) solutions were prepared by dissolving $Na_2Cr_2O_7 \cdot 2H_2O$ (Sigma-Aldrich) in water. In this paper, the total concentration of Cr(VI), $c_{Cr(VI)}$, is defined as follows:

$$c_{Cr(VI)} = [CrO_4{}^{2-}] + [HCrO_4{}^{-}] + 2[Cr_2O_7{}^{2-}] \quad (1)$$

The ionic strength was adjusted to $I = 1.0$ M by using appropriate amounts of $NaClO_4$ (Sigma Aldrich). Doubly deionized and ultrafiltered (Millipore Q system) water was used to prepare the stock solutions and the samples. The temperature was set to 25.0 °C in all experiments.

2.2. pH potentiometry

pH measurements were performed using a Metrohm 785 DMP Titrino automatic titrator equipped with a 6.0262.100 pH electrode. The electrode was calibrated every day using KH-phthalate (0.05 M) and borax (0.01 M) standard solutions. [16] The pH meter reading was converted into $pH_{calc} = -lg[H^+]$ as described earlier. [17]

2.3. UV–vis spectrophotometric titration

The speciation equilibria of Cr(VI) was studied by titrating acidic dichromate solutions with standardized NaOH solution in a home-built flow-through UV–vis and pH potentiometric titrating system (SI Fig. S1). After adding an aliquot of NaOH solution to the sample, the pH was measured and the spectrum of the solution was recorded in the 200–600 nm wavelength range in a flow-through cell with an HP-8453 diode array spectrophotometer equipped with an HP 89090A Peltier thermostat. The titrating vessel placed in a thermostated jacket and the optical cell were maintained at the same temperature by circulating water and using a Peltier heat exchanger, respectively.

2.4. Stopped-flow measurements

Fast kinetic experiments were carried out with an Applied Photophysics SX-20 stopped-flow instrument using a photomultiplier tube (PMT) attached as the detector. The kinetic traces were collected using optical cells of either 2.00 or 0.10 mm optical path length. The 0.10 mm cell is a custom made component of the instrument designed for studying species of high UV–vis absorption. In the current study, we work at relatively high Cr(VI) concentrations and the absorbances at the characteristic wavelengths are very high, thus, the standard 2.00 mm cell allows measurements only in a very limited wavelength range. Kinetic traces were obtained as the average of 2–5 runs in order to increase the signal-to-noise ratio. The dead time of the stopped-flow instrument was determined by monitoring the reduction of 2,6-dichlorophenol-indophenol (DCPIP) under pseudo-first order conditions with ascorbic acid (AA) in excess. [18] The dead time of the instrument was measured to be 1.51 ± 0.03 ms with the 2.00 mm cell, and 4.9 ± 0.2 ms with the 0.10 mm cell. In general, the dead time depends on the design of the instrument and the flow rate of the reactants, which is determined by the driving pressure of the driving ram. The 0.10 mm cell is custom made, and a driving pressure smaller than with the 2.00 mm standard cell was used to avoid rupturing (see SI). The difference of the corresponding dead times reflects mainly the different flow rates of the reactants. By plotting the experimentally obtained k_{obs} values against [AA] during the calibration, some deviation from linearity was observed above $k_{obs} = 600\ s^{-1}$ (in both cells), which means that higher k_{obs} values are unreliable. The experimental rate constants were far below this limit in this study.

3. Results and discussion

3.1. Speciation equilibria

The speciation equilibria of aqueous chromium(VI) was first studied by UV–vis spectrophotometric titration. Typical titration curves of acidic chromium(VI) solutions ($HClO_4$) are shown in Fig. 1. Five titrations were performed by using different total Cr(VI) concentrations from $c_{Cr(VI)} = 7.8$ mM to 77.7 mM. The first equivalence point at around pH 4 belongs to the neutralization of the excess $HClO_4$. At higher pH, a second equivalence point can be observed in all titration curves. The position of this equivalence point shifts as $c_{Cr(VI)}$ changes. This effect can be attributed to shifting the $HCrO_4^-/Cr_2O_7^{2-}$ dimerization equilibrium. A detailed explanation is given in the next paragraph.

The UV–vis spectra recorded during the titration of a $c_{Cr(VI)} = 7.8$ mM solution are shown in Fig. 2. Each spectrum corresponds to one point in the appropriate titration curve shown in Fig. 1. The absorbance as a function of pH is shown for a few selected wavelengths in Fig. 3. As expected, the absorbance does not change above pH 8 and below pH 4.

First, the multi-wavelength titration data were evaluated by matrix rank analysis (MRA). [19] The UV–vis spectra were collected from all pH titration experiments performed at different $c_{Cr(VI)}$ and compiled into a single data matrix. Thus, we ensured that all spectral effects introduced by changing pH and $c_{Cr(VI)}$ were simultaneously taken into account during data evaluation. The eigenvalues resulting from the MRA are given in Table S1 in the Supporting Information. The first three eigenvalues are in the same magnitude, all others are close to zero. These results suggest that three light absorbing species of different UV–vis spectra are present in the aqueous Cr(VI) solutions under the conditions applied. These are

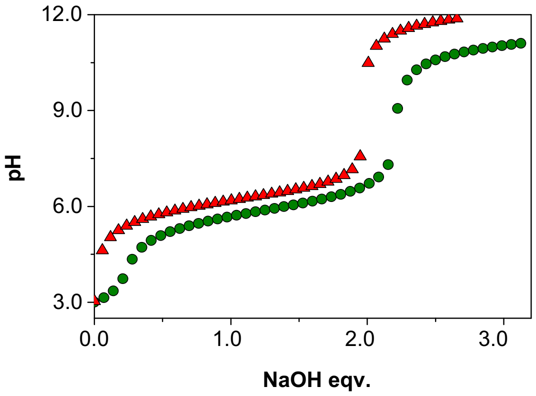

Fig. 1. The titration of acidic ($HClO_4$) $Na_2Cr_2O_7$ solutions with NaOH solution. Red trace (triangles): $c_{Cr(VI)} = 7.8$ mM; Green trace (dots): $c_{Cr(VI)} = 77.7$ mM, $I = 1.0$ M, $T = 25.0$ °C.

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