from 7 to 13 ml less than those of the starting materials. In order to provide a more detailed model, we have measured the partial molar volumes of sodium maleate and sodium malate and thereby obtained a value of −8.3 ml for the hydration of an unsaturated divalent ion. Several activation volumes for reactions involving the combination of an ion with a water molecule are available, and they lie in the range from −6 to −10 ml. Examples are the hydrolysis of epoxides[4a] and the hydration of olefins.[4b] The theoretical implications of these results are discussed in the references cited.

Another piece of information needed for the interpretation of the results is a knowledge of the volume change which would result from stretching of the Pt–Cl bond. Although specific information about this bond is not available, the activation volume for the decomposition of CCl_3^- into CCl_2 and Cl^- is reported to be +16 ml/mole.[10] Other unimolecular decompositions of univalent ions have positive values ranging up to 19 ml and averaging about 10 ml.[11]

In order to complete the formulation of a transition-state model it is necessary to postulate that the following physical processes are involved in greater or less degree. (1) One or more water molecules move inward and contribute to the formation of the Pt–OH_2 bond found in the product. (2) One of the Pt–Cl bonds elongates. We also postulate that the transition state has the same net charge as the original complex and constricts the same volume of solvent. It seems clear at the outset that the contribution of (2) is small since

the activation volume is strongly negative. If the coordination number of the Pt is not to rise above 6, the contribution of (1) is limited to an extreme of twice −8.3 ml (the volume of hydration of maleate ion), and this is nearly equal to the observed activation volume. If the previously mentioned dissociative mechanism is correct, then a structural representation of the mechanism which would be consistent with our data is as follows (X = NH_3 or Cl)
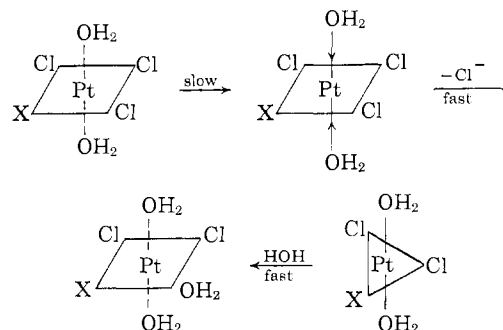
Other recent evidence which has a bearing on the transition-state structure is the determination of activation energies and entropies for these complexes.[12] The entropies for $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ are −16 and −23 eu. These values are consistent with a transition state in which increased bonding to the nucleophile is the dominant feature.

(11) K. R. Brower, B. Gay, and T. L. Konkol, *J. Am. Chem. Soc.*, **88**, 1681 (1966).

(12) U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

The Dissociation Equilibria of Trioxochlorochromate(VI) and Chromic Acid

By JAMES YINGPEH TONG and RAY L. JOHNSON

The equilibrium quotients of the reactions

$$CrO_3Cl^- + H_2O = HCrO_4^- + Cl^- + H^+$$
$$H_2CrO_4 = HCrO_4^- + H^+$$
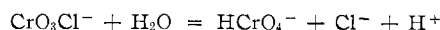
were determined spectrophotometrically at the wavelengths 320, 330, and 340 mμ at 15.0, 25.0, and 35.0° in solutions of unit ionic strength containing lithium perchlorate, lithium chloride, perchloric acid, and hydrochloric acid. The ΔH and ΔS of the dissociation of CrO_3Cl^- are −1.13 kcal and −8.6 eu, respectively. The ΔH and ΔS of the dissociation of H_2CrO_4 are −8.5 kcal and −26 eu, respectively.

The existence of trioxochlorochromate(VI) ion, CrO_3Cl^-, in solids has been known for many years. X-Ray studies have been reported on $KCrO_3Cl$[1,2] and on NH_4CrO_3Cl.[3] The reactions of $KCrO_3Cl$ have been in-

vestigated in liquid ammonia.[4-6] Chloro complexes have been postulated in the mechanism of oxidation of iso-

(1) S. Gawrych, *Roczniki Chem.*, **19**, 413 (1939).
(2) L. Helmholz and W. R. Foster, *J. Am. Chem. Soc.*, **72**, 4971 (1950).
(3) F. Hanic and J. Madar, *Chem. Zvesti*, **10**, 82 (1956).
(4) H. H. Sisler, *Trans. Kansas Acad. Sci.*, **46**, 136 (1943).
(5) H. H. Sisler and F. E. Jirik, *J. Am. Chem. Soc.*, **66**, 1344 (1944).
(6) S. I. Tannenbaum, R. S. Drago, and H. H. Sisler, *ibid.*, **79**, 1815 (1957).

propyl alcohol by Cr(VI) in 86.5% acetic acid and a formation equilibrium quotient has been reported.[7] The infrared spectrum of $KCrO_3Cl$ in Nujol mull and in acetone solution and the Raman spectrum of $KCrO_3Cl$ in aqueous hydrochloric acid solution have been determined.[8] The existence of $HCrO_3Cl$ in organic liquids was postulated in a solvent extraction study.[9] Two preliminary investigations of the equilibrium of CrO_3Cl^- in aqueous solutions have been reported.[10,11] The present work is a much more detailed study of the dissociation of CrO_3Cl^- in aqueous solutions which also yielded information on the first dissociation of chromic acid.

Experimental Section

The water used, the preparation and standardization of stock solutions of lithium perchlorate and perchloric acid, the spectrophotometric equipment, and the equipment for maintaining the solutions at constant temperature during spectrophotometric measurement were similar to those reported earlier.[12,13]

Primary standard grade (Mallinckrodt) potassium dichromate was dried at 110° before use. Other chemicals were of reagent grade. Hydrochloric acid stock solutions were prepared by diluting more concentrated solutions and were standardized volumetrically with standard 1 M sodium hydroxide solutions. Lithium chloride was recrystallized once from water, and its stock solution was standardized volumetrically with a standard silver nitrate solution.

Preparation of Solutions for Spectrophotometric Measurement. —The stock solutions were added to 100-ml volumetric flasks in the following order: hydrochloric acid, perchloric acid, lithium chloride, and lithium perchlorate. A calculated volume of water was added so that when chromium(VI) stock solution was added, the total volume would be just under 100 ml. The chromium-(VI) stock solution was not added until immediately before spectrophotometric measurements were to be made. The final dilution to volume was done with the volumetric flask partially immersed in the 25.0° water bath.

Stability of the Solutions Measured. —The above precautions were taken to avoid the prolonged contact of chromium(VI) with chloride ions and hydrogen ions at concentrations much greater than those in the final solutions which were 1 M or less. Solutions of chromium(VI) containing more than 1 M hydrogen ion were reported to change slowly to chromium(III).[11] The stability of the solutions measured was tested in two ways. First, a solution of 5.41×10^{-5} M chromium(VI) in 1.0 M hydrochloric acid was prepared and kept at 45° in a 10-cm spectrophotometric cell. No change in absorbance was observed after 1 day and a decrease of less than 0.5% was observed after 2 days. Since all absorbances were measured at lower temperatures within 3–4 hr from the time the solutions were prepared, it was concluded that chromium(VI) reduction was too slow to cause error. The absorbances of the solutions were measured in the order 15.0, 25.0, and 35.0°. As a further test of stability, the solutions were cooled from 35.0 to 15.0° and the 15.0 and 25.0° measurements were repeated and were found to be reproducible to within ±0.5%.

Five series of solutions of unit ionic strength and of hydrogen ion concentrations 0.2, 0.3, 0.4, 0.6, and 1.0 M were prepared. The chromium(VI) concentration was 5.00×10^{-5} M in the first series and 4.69×10^{-5} M in the last three series. In each series

(7) M. Cohen and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4387 (1952).

(8) H. Stammerich, O. Sala, and K. Kawai, *Spectrochim. Acta*, **17**, 226 (1961).

(9) D. G. Tuck and R. M. Walters, *J. Chem. Soc.*, 1111 (1963).

(10) O. Lukkari, *Suomen Kemistilehti*, **B35**, 91 (1962).

(11) G. P. Haight, Jr., D. C. Richardson, and N. H. Colburn, *Inorg. Chem.*, **3**, 1777 (1964).

(12) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

(13) J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964).

the chloride ion concentrations were 0, 0.2, 0.3, 0.5, 0.8, and 1.0 M. The solutions containing no chloride ion were made in duplicate. Thirty blank solutions of similar composition but without chromium(VI) were prepared. The concentrations at 15.0 and 35.0° were calculated by multiplying the 25.0° concentrations by the factors 1.002 and 0.997, respectively, by assuming that the solutions used had thermal expansion coefficients similar to those of water.

Spectrophotometric Measurements. —The wavelength scale of the Beckman DU spectrophotometer was calibrated with mercury-emission lines and was found to be within the specifications of the manufacturer. Cylindrical cells of 10.00-cm light path length were used. The slit widths used were 0.22, 0.15, and 0.12 mm at wavelengths 320, 330, and 340 mμ, respectively. The temperature of the solution during the measurement was within ±0.1° of the stated temperature. The 315 net absorbance values determined were all within the range of 0.2 and 0.72 with only 70 values (mostly at 320 mμ) in the range of 0.2 and 0.3.

Results and Discussion

Interpretation of Data at One Hydrogen Ion Concentration. —Since the hydrogen ion and chloride concentrations were always much greater than the chromium-(VI) concentration (by a factor of 4×10^3 or greater), it was assumed that the concentrations of these species were equal to their stoichiometric concentrations. At the stoichiometric concentrations of chromium-(VI) used, the amount of dimeric chromium(VI) species was negligible and the principal species were $HCrO_4^-$ and H_2CrO_4. It was assumed that chloride ions formed only 1:1 complexes with chromium(VI), most likely CrO_3Cl^- and $HCrO_3Cl$.

At a given hydrogen ion concentration the concentration ratios $(HCrO_4^-)/(H_2CrO_4)$ and $(CrO_3Cl^-)/(HCrO_3Cl)$ are constant and the total concentrations of complexed and uncomplexed chromium(VI), c_2 and c_1, are proportional to the concentrations (CrO_3Cl^-) and $(HCrO_4^-)$, respectively. The dissociation of the complex ions may be represented by a gross equilibrium quotient, K_G, in terms of the total concentrations, where

$$K_G = (\text{uncomplexed Cr(VI)})(Cl^-)/(\text{complexed Cr(VI)}) \quad (1)$$

$$= c_1(Cl^-)/c_2$$

The observed absorbance, A, of a solution due to species containing chromium(VI) in a cell of light path length b cm is related to the apparent absorptivity, ϵ, of the solution and the apparent molar absorptivities, ϵ_2 and ϵ_1, of the complexed and uncomplexed chromium(VI) species by

$$A/b = \epsilon(c_1 + c_2) = \epsilon_1 c_1 + \epsilon_2 c_2 \quad (2)$$

At each hydrogen ion concentration, the apparent molar absorptivities of uncomplexed monomeric chromium(VI), ϵ_1, were determined with solutions containing no chloride ions. Because of the importance of this quantity, duplicate solutions were prepared and measured and the average values were used. The values of ϵ_1 are given in Table I.

Elimination of c_1 and c_2 between eq 1 and 2 and rearrangement result in

$$(Cl^-)/(\epsilon_1 - \epsilon) = [K_G/(\epsilon_1 - \epsilon_2)] + [(Cl^-)/(\epsilon_1 - \epsilon)] \quad (3)$$

Table I

Apparent Molar Absorptivity of Monomeric Chromium(VI)

(H$^+$), M	Temp, °C	ϵ_1, M^{-1} cm^{-1}		
		320 mμ	330 mμ	340 mμ
1.002	15.0	767	1079	1376
0.601	15.0	779	1101	1408
0.401	15.0	787	1111	1421
0.301	15.0	787	1116	1427
0.2005	15.0	792	1116	1427
1.000	25.0	758	1062	1358
0.600	25.0	768	1084	1388
0.400	25.0	778	1098	1405
0.300	25.0	778	1104	1408
0.200	25.0	780	1100	1414
0.997	35.0	749	1047	1342
0.598	35.0	759	1066	1368
0.399	35.0	770	1086	1387
0.299	35.0	772	1091	1390
0.1994	35.0	774	1093	1402

According to eq 3, a graph of $(Cl^-)/(\epsilon_1 - \epsilon)$ *vs.* (Cl^-) will be a straight line as in Figure 1 with slope $1/(\epsilon_1 - \epsilon_2)$ and intercept $K_G/(\epsilon_1 - \epsilon_2)$ from which K_G may be calculated. The present data were treated numerically by the method of least squares with eq 3 using an IBM 1620 digital computer. The K_G values are given in Table II.
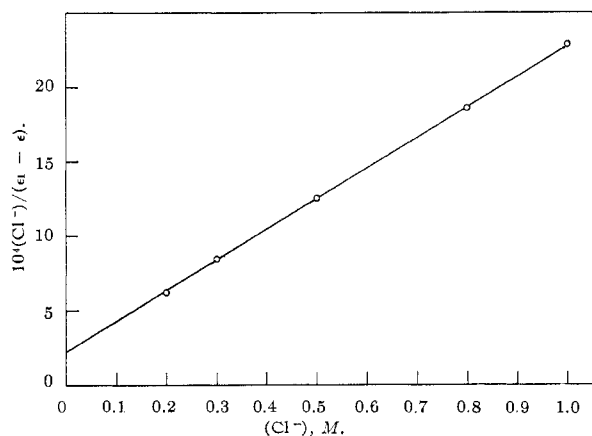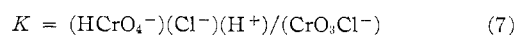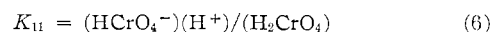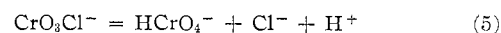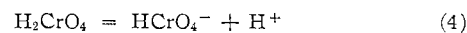

Figure 1.—$(Cl^-)/(\epsilon_1 - \epsilon)$ *vs.* (Cl^-) at 1.000 M (H$^+$), 25.0°, and 330 mμ.

Table II

Gross Equilibrium Quotients K_G

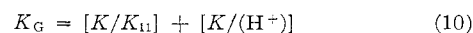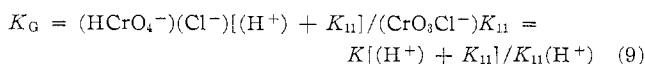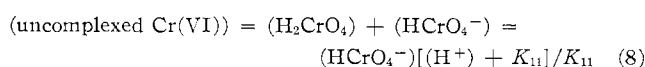| (H$^+$), M	Temp, °C	K_G, M		
		320 mμ	330 mμ	340 mμ
1.002	15.0	0.107	0.104	0.109
0.601	15.0	0.158	0.152	0.166
0.401	15.0	0.252	0.248	0.263
0.301	15.0	0.325	0.301	0.326
0.2005	25.0	0.466	0.473	0.477
1.000	25.0	0.109	0.109	0.116
0.600	25.0	0.159	0.157	0.168
0.400	25.0	0.254	0.259	0.267
0.300	25.0	0.332	0.322	0.315
0.200	25.0	0.468	0.457	0.474
0.997	35.0	0.113	0.113	0.118
0.598	35.0	0.157	0.156	0.164
0.399	35.0	0.242	0.234	0.245
0.299	35.0	0.314	0.296	0.310
0.1994	35.0	0.436	0.423	0.447

Hydrogen Ion Concentration Dependence.—The values of K_G were found to decrease with increasing hydrogen ion concentrations. This could be explained by assuming that the predominant species of the complex was CrO_3Cl^- and that the principal equilibria in solution and their equilibrium quotients were

$$H_2CrO_4 = HCrO_4^- + H^+ \tag{4}$$

$$CrO_3Cl^- = HCrO_4^- + Cl^- + H^+ \tag{5}$$

$$K_{11} = (HCrO_4^-)(H^+)/(H_2CrO_4) \tag{6}$$

$$K = (HCrO_4^-)(Cl^-)(H^+)/(CrO_3Cl^-) \tag{7}$$

Since

$$(\text{complexed Cr(VI)}) = (CrO_3Cl^-)$$

and

$$(\text{uncomplexed Cr(VI)}) = (H_2CrO_4) + (HCrO_4^-) = (HCrO_4^-)[(H^+) + K_{11}]/K_{11} \tag{8}$$

$$K_G = (HCrO_4^-)(Cl^-)[(H^+) + K_{11}]/(CrO_3Cl^-)K_{11} = K[(H^+) + K_{11}]/K_{11}(H^+) \tag{9}$$

$$K_G = [K/K_{11}] + [K/(H^+)] \tag{10}$$
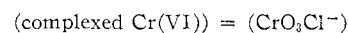
According to eq 10, K_G will decrease with increasing hydrogen ion concentration, (H$^+$), and a graph of K_G *vs.* $1/(H^+)$ will be a straight line with intercept K/K_{11} and slope K as in Figure 2. The slope and intercept at each temperature were calculated by the method of least squares with eq 10 using all 15 values of K_G at the same time. The values of K and K_{11} calculated from the slopes and intercepts are given in Table III.
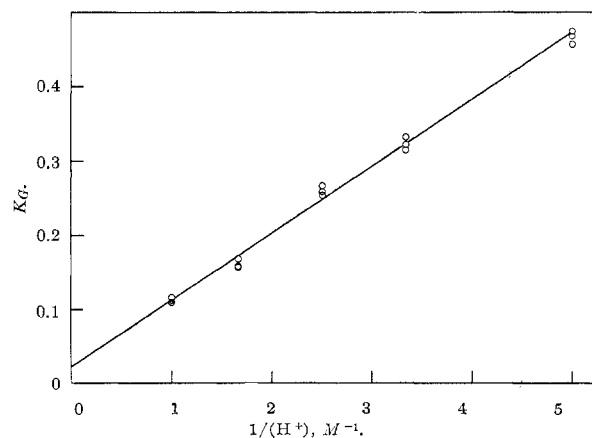

Figure 2.—K_G *vs.* $1/(H^+)$ at 25.0° and three wavelengths. Double circle indicates identical values. Radius of circle is 0.004 unit on the K_G scale.

Table III

Equilibrium Quotients K and K_{11} and the Average Molar Absorptivities of CrO_3Cl^-, ϵ_2

	Temp, °C		
	15.0	25.0	35.0
K, M^2	0.0917	0.0901	0.0806
K_{11}, M	6.8	4.1	2.6
Av ϵ_2 (320 mμ)	395 ± 7.2[a]	284 ± 6.0	381 ± 6.3
Av ϵ_2 (330 mμ)	597 ± 8.7	576 ± 7.7	570 ± 7.9
Av ϵ_2 (340 mμ)	870 ± 12.4	845 ± 10.7	838 ± 13.2

[a] The number following each ϵ_2 is its standard deviation.

The molar absorptivities of CrO_3Cl^-, ϵ_2, were calculated from the observed absorptivities of all the solutions using the values of K and K_{11} from Table III. Each ϵ_2 value at a given temperature and wavelength given in Table III is the average of 25 values at all hydrogen ion concentrations and chloride ion concentrations used. The ϵ_2 values were independent of the hydrogen ion and chloride ion concentrations and gave no evidence of the presence of $HCrO_3Cl$.

Comparison with Previous Works on Trioxochlorochromate(VI) Dissociation.—For convenience in comparison, the equilibrium quotients reported in previous works to be quoted are converted to expressions used in the present work. Cohen and Westheimer[7] gave a K value of 0.901×10^{-5} M^2 determined spectrophotometrically at 255, 380, and 390 mμ and a value of 1.0×10^{-5} M^2 calculated from the effect of chloride ion on the rate of oxidation of isopropyl alcohol by chromium(VI) in 96.5% acetic acid of ionic strength 0.125 M at 0.3°. Since the medium used was very different, no direct comparison is possible.

Lukkari[10] reported a K value of 0.117 M^2 at 20° in solutions of unit ionic strength maintained with sodium perchlorate. He corrected his chromium(VI) concentration for the dichromate ion concentration using a chromium(VI) dimerization equilibrium constant of 128 M^{-1} which was too large since K_d was found to be 113 M^{-1} at 15.0°.[14] The overcorrection for dichromate ion concentration was compensated for in part by not correcting for H_2CrO_4 concentration which was not mentioned. The latter correction based on the interpolated K_{11} value of the present study of 5.2 M amounted to only 2% at the highest hydrogen ion concentration used which was 0.1 M. His K value is in very good agreement with the value of 0.111 M^2 calculated by interpolation from the present data.

Haight, *et al.*,[11] using data at 260, 320, and 350 mμ determined a K_G value of 0.071 M (reciprocal of their K_{obsd} value) at 25° in sodium perchlorate solutions of unit ionic strength containing 1 M hydrogen ion. The corresponding value determined in the present study was 0.111 M. They assumed that in a 1 M hydrochloric acid solution all of the chromium(VI) was complexed and used the apparent absorptivity of such a solution as the molar absorptivity of CrO_3Cl^-, ϵ_2. According to the present data, only 90% of chromium(VI) was complexed in a 1 M hydrochloric acid solution at 25.0°. The ϵ_2 they used was, therefore, too large and their K_G value too small. At 320 mμ their ϵ_2 value of 423 M^{-1} cm^{-1} agreed with the apparent absorptivity value of 421 M^{-1} cm^{-1} in a 1 M hydrochloric acid solution measured in the present study but was much greater than the true ϵ_2 value of 384 M^{-1} cm^{-1}. Using the latter value, a K_G value of $0.10_4 \pm 0.014$ M could be calculated from their data at 320 mμ.

Holloway[15] reported a value of 9 M^{-1} for the equilibrium quotient of the reaction

$$HCrO_4^- + H_3PO_4 = H_2CrPO_7^- + H_2O \qquad (11)$$
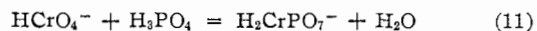
in sodium perchlorate solutions of 0.25 M ionic strength at 25°. Using their calculated value of 0.0135 M of the first dissociation quotient of phosphoric acid, one could calculate an equilibrium quotient of 0.0015 M^2 of the reaction

$$H_2CrPO_7^- + H_2O = HCrO_4^- + H_2PO_4^- + H^+ \qquad (12)$$
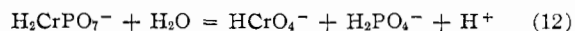
Comparison of the equilibrium quotients of reactions 12 and 5 showed that $H_2CrPO_7^-$ was more stable than CrO_3Cl^-.

Haight, *et al.*,[11] reported an equilibrium quotient of 0.24 M for the reaction

$$CrSO_7^{2-} = HSO_4^- + HCrO_4^- \qquad (13)$$

at ionic strength 3.0 and 25°. The hydrogen ion concentration was not given and no mention was made of whether they corrected for the dissociation of HSO_4^- and H_2CrO_4. They reported that the solutions had the same absorbance from 15 to 35° and concluded that ΔH of reaction 13 was zero.

From the present data the ΔH and ΔS of the dissociation of CrO_3Cl^- ion according to eq 5 were -1.13 kcal and -8.6 eu, respectively. No such data on other reactions of chromium(VI) involving ions of the same charges are available for comparison.

Comparison with Previous Work on the Dissociation of Chromic Acid.—The present value of K_{11} of 4.1 M at 25.0° is in excellent agreement with the previous value of 4.16 M determined in the same medium.[13] The interpretation which led to the smaller value of 1.21 M^{12} was discussed before.[13] The use of the K_{11} value of 1.21 M to account for the hydrogen ion concentration dependence of K_G required the assumption that the species $HCrO_3Cl$ existed in solution with an acid dissociation quotient K_1. The equilibrium quotients calculated at 25.0° with $K_{11} = 1.21$ M were $K = 0.089$ M^2 and $K_1 = 2.1$ M. Since the larger K_{11} values accounted well for the present data and since experimental evidence for the existence of $HCrO_3Cl$ was not available, the interpretation without the use of $HCrO_3Cl$ was considered valid.

Shevcenko, *et al.*,[16] reported a K_{11} value of 1.26 M obtained from the hydrogen ion concentration dependence of the distribution quotient of chromium(VI) between an aqueous acidic solution and a benzene solution of tributyl phosphate. Recalculation of their data by the method of least squares gave a value of 1.64 M. Not enough experimental detail was given to permit a thorough evaluation.

The K_{11} values reported by Haight, *et al.*,[11] have been discussed elsewhere.[13] They estimated ΔH and ΔS of the first dissociation of chromic acid to be -2.1 kcal and 2.5 eu from the change of absorbance of

(14) J. Y. Tong and B. R. Kokenge, to be published.

(15) F. Holloway, *J. Am. Chem. Soc.*, **74**, 224 (1952).

(16) V. B. Shevcenko, I. V. Shilin, and Yu. K. Zhdavov, *Zh. Neorgan. Khim.*, **5**, 2832 (1960).

chromium(VI) in a 3 M perchloric acid solution as temperature was changed from 17 to 32°. From the present data the ΔH and ΔS of the first dissociation of chromic acid were -8.5 kcal and -26 eu, respectively. The ΔS value was of the same order of magnitude as ΔS values of other weak acids.[17,18]

(17) E. L. King, *J. Chem. Educ.*, **30**, 71 (1953).
(18) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y. 1958, p 667.

The Exchange Rates of Water and Thiocyanate Ion With Nickel(II)–Thiocyanate Complexes by Oxygen-17 and Nitrogen-14 Nuclear Magnetic Resonance[1,2]

By R. B. JORDAN, HAROLD W. DODGEN, and JOHN P. HUNT[3]

Water and thiocyanate exchange rates have been measured for aquothiocyanato complexes of nickel(II) ($[Ni(NCS)_4(H_2O)_2]^{2-}$ presumably) in concentrated aqueous thiocyanate solutions. These exchanges proceed independently over the temperature range studied. In *ca.* 8 M KNCS, ΔH^* for water exchange is 6.0 ± 0.6 kcal/mole while ΔH^* for thiocyanate exchange is 9.2 ± 0.6 kcal/mole. In 3.5 M NaNCS plus 4.5 M NaClO$_4$, ΔH^* for water exchange is 7.4 ± 0.5 kcal/mole. The scalar coupling constant A/h for H$_2$O^{17} in $[Ni(NCS)_4(H_2O)_2]^{2-}$ is 2.0×10^7 cps. Substitution of water in $[Ni(H_2O)_6]^{2+}$ by thiocyanate results in a labilizing of the remaining water ligands.

Introduction

Some preliminary results were reported earlier on H$_2$O^{17} exchange with a presumed $[Ni(NCS)_4(H_2O)_2]^{2-}$ species.[4] These suggested that water and thiocyanate exchange proceeded independently and led us to investigate the matter in more detail. Such studies may give new insight into the mechanisms of substitution reactions in complex ions.

Experimental Section

The nmr techniques and equipment previously described have been used.[4,5] Using a static field of 9270 gauss, the O^{17} nmr line in H$_2$O was observed at *ca.* 5.35 Mc/sec while the N^{14} line in aqueous KNCS solution occurs at *ca.* 2.85 Mc/sec. Much better control of the sample temperature in the nmr probe than was previously possible was achieved by circulating thermostated isooctane or pentane through the probe rather than nitrogen gas. Sample temperatures were constant to $\pm0.1°$ throughout the sample.

Solutions were prepared using water containing 1.19 atom % O^{17} (*ca.* 17% O^{18} and "normalized" in H content) obtained from Bio-Rad Laboratories. Water redistilled from alkaline permanganate gave the same results as the water used as supplied. Other reagents used were Fisher Scientific Co. CP Ni(NO$_3$)$_2$·6H$_2$O, Baker Analyzed KNCS, and NaClO$_4$ prepared by the method of Willard and Smith.[6]

Measurements of O^{17} chemical shifts (S) were made using, for reference purposes, a small sample tube containing KNCS in H$_2$O^{17} placed inside the usual sample tube and solution.

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Treatment of Data and Results

The basic theoretical treatment is found in the detailed paper of Swift and Connick.[7] Some modifications of this treatment were subsequently introduced by our group.[8] The details are somewhat involved and will not be repeated here except in outline. We are concerned with line broadenings for the free H$_2$O^{17} and N^{14}CS$^-$ nmr absorption signals produced by the addition of paramagnetic Ni(II). Line broadening results are reported in terms of the quantity $T_{2p}'' = 2\,m(Ni)/\gamma\Delta'$ where $m(Ni)$ is the total molality of Ni(II), γ is the magnetogyric ratio (3628 gauss^{-1} sec^{-1} for O^{17} and 1934 gauss^{-1} sec^{-1} for N^{14}), and Δ' is the line broadening in gauss, measured at half-maximum absorption using the full line widths, produced by added Ni(II). That is, Δ' is ($W_{obsd} - W_0$) where W_{obsd} is the line width observed in the presence of Ni(II) and W_0 is the line width observed at the same temperature and other conditions except with no added nickel. Values for Δ', T_{2p}'', and W_0 as a function of temperature and composition of the solutions are given in Table I. Values of Δ' are the average of three or four measurements and have a precision of ±5–10%. A semilogarithmic plot of TT_{2p}'' (T = absolute temperature) *vs.* $10^3/T$ is given in Figure 1.

The shift data for H$_2$O^{17} are given in Table II and are plotted in Figure 1. The quantity $TSm(H_2O)/m(Ni)$ is used where S is the change in frequency divided by the original frequency and $m(H_2O)$ is the molality of the water.

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