

Kinetics of Complex Formation

I*. The Chromium(III)-thiocyanate System

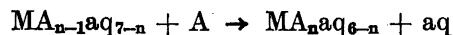
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A study of the chromium(III)-thiocyanate complexes has been made in a controlled salt medium. The equilibrium constants for the uptake of the 1st and 2nd thiocyanate ion, together with the rate constant for the uptake of the 1st thiocyanate ion have been estimated at 25, 50 and 75° C by means of an argentometric determination of the concentration of the free thiocyanate ion. The rate constant for the dissociation of the 1st thiocyanate ion from the hexa-thiocyanate complex has been estimated at 15 and 25° C by a spectrophotometric method. From the temperature dependence of the constants, the activation energies and frequency factors as well as the changes in enthalpy and entropy for the reactions in question are calculated.

The chromium(III) ion exists in aqueous solution as a hexaquo ion², and it is characteristic that chromium(III) complexes are usually formed by slow time reactions. The thiocyanate system was investigated by Niels Bjerrum³, who showed that all six possible complexes were formed. N. Bjerrum worked out elegant methods to determine the concentration of the individual complexes, and estimated all the 6 equilibrium constants at 50° C. He also gave approximate values for the rate of aquation of all the complexes with the exception of the dithiocyanato complex.

Let us for the bimolecular formation reaction



denote the velocity constant, frequency factor and activation energy by k_n , Z_n and E_n , and for the corresponding pseudo-unimolecular dissociation reaction



* The numerical values given in the present paper supercede those presented in a preliminary communication by J. Bjerrum at the 7th »Nordiska Kemistmötet», Helsinki 1950 (cf. ref. 1).

by k_{-n} , Z'_{-n} ($= Z_{-n} \cdot C_{aq}$) and E_{-n} , respectively. According to the Arrhenius equation we then have for the uptake of the n 'th ligand

$$\log k_n = \log Z_n - \frac{E_n}{2.3 RT}; \quad (1)$$

for the dissociation of the n 'th ligand

$$\log k_{-n} = \log Z'_{-n} - \frac{E_{-n}}{2.3 RT}; \quad (2)$$

and for the equilibrium constant

$$\log K_n = \log \frac{k_n}{k_{-n}} = \log \frac{Z_n}{Z'_{-n}} + \frac{E_{-n} - E_n}{2.3 RT}. \quad (3)$$

Denoting the heat and entropy for the uptake of the n 'th ligand by ΔH_n and ΔS_n , respectively, the consecutive formation constant is also given by the formula:

$$\log K_n = \frac{\Delta S_n}{2.3 R} - \frac{\Delta H_n}{2.3 RT} \quad (4)$$

where

$$\Delta H_n = E_n - E_{-n} \quad (5)$$

and

$$\Delta S_n = 2.3 R \log \frac{Z_n}{Z'_{-n}} \quad (6)$$

In the present paper some of the reactions in the system are studied in controlled neutral salt medium and at different temperatures. Data for the examined reactions are given in Table 1. The complex formation was followed by determination of the free thiocyanate by titration with silver nitrate. Using this method the formation velocity constant k_1 and the consecutive complexity constants K_1 and K_2 could be obtained. The two first mentioned of these constants indirectly also determine k_{-1} , the dissociation velocity constant of the monothiocyanate complex. The dissociation reactions of the thiocyanate chromium complexes are with the exception of the hexathiocyanato complex

Table 1. Comparison of thermodynamic and kinetic results*.

n	$\log K_n$ (25°)	$-\Delta H_n$ (kcal)	$\Delta S_n/2.3 R$	Medium
1	1.87 ± 0.01	1.4 ± 0.2	0.8 ± 0.2	1 M NaClO ₄
2	1.11 ± 0.07			,
	$\log k_n$ (25°)	E_n (kcal)	$\log Z_n$	
1	-5.21 ± 0.03	25.0 ± 0.3	13.2 ± 0.2	,
1	-4.5 (calc.)	21.4 ± 0.3	11.2 ± 0.2	$\mu = 0.1$
	$\log k_{-n}$ (25°)	E_{-n} (kcal)	$\log Z'_{-n}$	
1	-7.08 ± 0.04	26.5 ± 0.4	12.4 ± 0.3	1 M NaClO ₄
6	-4.662 ± 0.004	25.4 ± 0.5	14.0 ± 0.3	,
6	-4.634 ± 0.002	25.7 ± 0.3	14.3 ± 0.2	$\mu = 0.1$

* Concentrations in moles per liter and time in seconds.

strongly catalyzed by hydroxyl ions as shown by N. Bjerrum³, but as k_1 is independent of the hydrogen ion concentration, the computed value for k_{-1} must be the dissociation velocity constant for the pentaquo-monothiocyanato chromium ion. The aquation velocity constant for the hexathiocyanato ion (k_{-6}) was determined by spectrophotometric estimation of the free thiocyanate after addition of ferric salt.

For a reaction between a trivalent and a monovalent ion of opposite charges one should expect a frequency factor essentially higher than the normal value for a bimolecular reaction ($\log Z \sim 11$). It will be seen that the value found for $\log Z_1$ only in 1 *M* NaClO₄ is higher, but not nearly as high as assumed by some authors. Moelwyn-Hughes⁴ and Frost and Pearson⁵ use N. Bjerrum's values for k_1 (at two temperatures), and estimate $\log Z_1 = 19.5$, but Bjerrum's values are only rough estimates and were never meant to be used for such a calculation. On the other hand, for the aquation of the thiocyanate complexes one should expect a normal frequency factor. The value found for $\log Z_{-6}$ seems rather high, but taking into consideration that $C_{H_2O} = 55$, one estimates $\log Z_{-1} = 10.7$ and $\log Z_{-6} = 12.3$. A considerable salt effect is to be expected on k_1 in agreement with the experimental results. E_1 and $\log Z_1$ are seen both to decrease with increasing salt concentration. Conversely, there should be no salt effect on the aquation reactions as experimentally verified for k_{-6} .

Our values for the complexity constants are smaller than those determined by N. Bjerrum in solutions of varying salt concentration, but this correlates well with the kinetic salt effect found on k_1 (see Table 2, in which Bjerrum's⁶ roughly approximated values to $\mu = 0$ are also given).

Table 2. Comparison of complexity constants at 50° C.

n	This paper log K_n (1 <i>M</i> NaClO ₄)	N. Bjerrum ⁶ log K_n	Salt- Normality	log K_n ($\mu = 0$)
1	1.79 ± 0.01	2.51	0.04–0.06	3.1
2	1.0 ± 0.05	1.24	0.06–0.2	1.7
3		0.66	0.1–2.0	1.0
4		0.29	0.7–4.5	0.3
5		–0.09	3.0–4.5	–0.7
6		–0.39	4.5	–1.6

Assuming $\log K_6 \sim -0.4$ in molar solution at 25° we estimate $\log k_6 \sim -5.0$. This shows that the trend in the complexity constants, which N. Bjerrum⁶ accounted for on statistical and electrostatic grounds, is mainly refound in the velocity constants for the aquation reactions, and here again it is especially the activation entropy, *i.e.* $\log Z$, which increases with the number of complex-bound thiocyanate ions.

EXPERIMENTAL

A stock solution of sodium perchlorate was made by neutralizing perchloric acid solution (Bakers A. R.) with sodium hydroxide solution.

Sodium thiocyanate solutions were made from recrystallized sodium thiocyanate (Merck purum).

Chromium(III) perchlorate was made by dissolving chromium hydroxide (Riedel de Haën puriss.) in perchloric acid solution. The 0.2 molar stock solution was weakly acidic (pH = 1.45). By spectrophotometric comparison with an acid chromium(III) nitrate solution made from crystallized chromic nitrate it was shown to be practically free of latently basic chromium compounds⁷. After three years at room temperature this was shown still to be the case while the originally soluble chromic hydroxide in the meantime had been converted into an insoluble latently basic form.

Potassium hexathiocyanato chromate(III) was made according to Roesler⁸ by boiling chromic alum with an excess of potassium thiocyanate in concentrated solution. After completion of the reaction K_2SO_4 was precipitated by mixing with ethanol, and filtered off. By staying at room temperature, crystals of $K_2Cr(SCN)_6 \cdot 4 H_2O$ separated from the filtrate. After 3 recrystallisations from water-ethanol, a very pure salt was obtained — no free thiocyanate was observed by the iodide-azide reaction (this seems to indicate, incidentally, that the ligands are attached to the chromium atom by the sulphur atom). Analysis gave results corresponding very well to the theoretical formula.

Chromium concentrations were determined by oxidizing the sample with ammonium persulphate in approx. 1 N sulphuric acid solution in the presence of Ag^+ , boiling off excess of persulphate, and after cooling, titrating the chromium(VI) with ferrous ammonium sulphate solution using diphenylamine-sulphonate as redoxindicator. Phosphoric acid was added to eliminate the colour of ferric ions formed.

Thiocyanate concentrations were determined by titration with standard silver nitrate solution using ferric sulphate as indicator.

All experiments were carried out in a thermostated bath, closed from light to avoid possible photochemical reactions. The temperature could be kept constant within $\pm 0.02^\circ C$.

ESTIMATION OF EQUILIBRIUM CONSTANTS.

N. Bjerrum³ examined solutions of chromic nitrate and potassium thiocyanate to which no excess of free acid was added. The chromic salt, therefore, was partly hydrolyzed and considerable amounts of polynuclear basic compounds were formed during the equilibrium adjustment⁷. To escape N. Bjerrum's cumbersome corrections for latently basic compounds we have examined solutions which were 0.02 molar in free perchloric acid, paying due regard to the fact that thiocyanate ions are not stable in strongly acid solution. To show that the slow hydrolysis is negligible at this acid concentration a solution of the composition $C_{Cr(ClO_4)_3} = 0.02$, $C_{HClO_4} = 0.02$ was heated to $75^\circ C$ in 24 hours. After cooling it was found that the conductance had risen about 1 % and that $-\log [H^+]$ had changed from 1.70 to 1.69. Heating to $75^\circ C$ for three more days had very little influence on the acidity. At $50^\circ C$ latently basic compounds are formed to a much smaller extent (*cf. ref. 7, p. 126*).

The chromium thiocyanate solutions used in the equilibrium experiments were mixed from the stock solutions and placed in the thermostat in 100 ml glass-stoppered bottles covered with rubber sheets. The equilibrium was reached after approx. 2 weeks at $25^\circ C$ and some hours at $75^\circ C$.

From the equilibrium solutions samples were pipetted into ice-cooled Erlenmeyer flasks containing an excess of silver nitrate solution. In this way — by freezing the complex reactions in the system — it was possible to estimate the free thiocyanate concentration $[SCN^-]$ by titration of the excess silver nitrate with standard sodium thiocyanate solution using a semi-micro burette.

The total chromium concentration (C_{Cr}) was determined from another sample, which was boiled for some minutes with a small excess of ammonium hydroxide³. The precipitated basic chromium compounds were filtered off

and washed, and the chromium determined by the method described above. In the bulk of the filtrate and washing water the total thiocyanate concentration (C_{SCN^-}) was determined. The experimental data, therefore, give directly the formation function:

$$\bar{n} = \frac{C_{\text{SCN}^-} - [\text{SCN}^-]}{C_{\text{Cr}}} \quad (7)$$

In the solutions with greater complex formation, detection of the endpoint in the Volhard-titration became difficult, because the reddish colour of the complexes covered the indicator system³. Due to this and also because we cannot consider the salt medium as constant when $C_{\text{SCN}^-} \lesssim 0.1$, only the 1st and 2nd formation constants could be determined with reasonable certainty.

The constants were estimated by a graphical procedure similar to that described by Olerup⁹. To this purpose we introduce the function

$$G_1([A]) = \frac{\bar{n}}{[A]} = K_1(1 - \bar{n}) + \sum_{n=2}^{n=N} (n - \bar{n})\beta_n[A]^{n-1} \quad (8)$$

where $\beta_n = K_1 K_2 \dots K_n$, and in this case $N = 6$ and $[A] = [\text{SCN}^-]$. Graphical representation of $G_1([\text{SCN}^-])$ versus the free ligand concentration and extrapolation to $[\text{SCN}^-] = 0$ gives K_1 directly. Table 3 presents the results obtained

Table 3. Data for equilibrium solutions in 1 M sodium perchlorate.

Temperature	No.	C_{Cr} $\times 10^3$	C_{SCN^-} $\times 10^3$	$[\text{SCN}^-]$ $\times 10^3$	\bar{n}	$\frac{\bar{n}}{[\text{SCN}^-]}$
25°	1	12.25	4.187	2.321	0.152	65.6
25°	2	15.05	5.899	3.027	0.191	63.1
25°	3	16.06	7.299	3.754	0.223	60.0
25°	4	15.79	8.467	4.415	0.257	58.3
25°	5	16.81	9.939	5.170	0.284	55.9
50°	6	15.19	1.571	0.825	0.049	59.3
50°	7	18.32	3.057	1.561	0.082	56.7
50°	8	18.04	4.739	2.388	0.131	54.7
50°	9	18.20	6.202	3.142	0.165	52.6
50°	10	19.44	7.774	3.904	0.199	51.0
50°	11	20.45	10.677	5.384	0.259	48.0
75°	12	22.04	6.404	3.241	0.147	45.5
75°	13	22.78	7.405	3.729	0.163	43.5
75°	14	23.70	9.184	4.643	0.193	41.7
75°	15	25.39	10.014	5.044	0.196	38.9
75°	16	24.61	10.773	5.425	0.217	40.0

at 25°, 50° and 75° for concentrations of free ligand up to $\sim 0.005 M$, and in Fig. 1 their graphical representation is seen. From the intersection of the curves and the ordinate axis are found

$$K_1(25^\circ) = 74 \pm 1, K_1(50^\circ) = 61.5 \pm 1, K_1(75^\circ) = 52 \pm 2.$$

It is also possible to estimate the value of K_2 from the curves. Differentiation of (8) with respect to $[A]$ gives for the slope at the origin

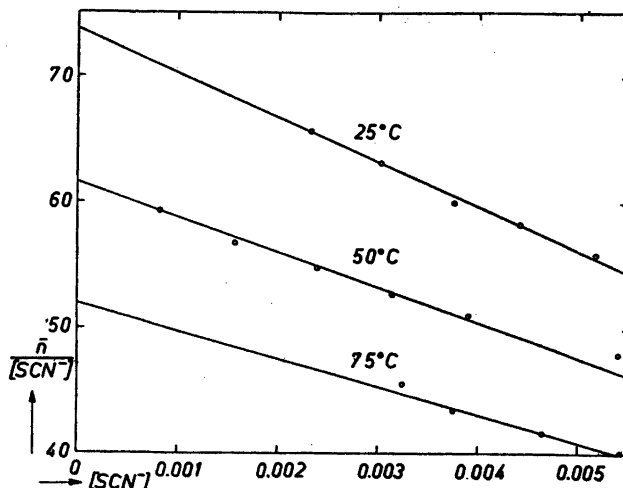


Fig. 1. Graphical estimation of K_1 as the value of $\frac{\bar{n}}{[\text{SCN}^-]}$ for $[\text{SCN}^-] = 0$.

$$\left(\frac{dG_1[\text{A}]}{d[\text{A}]}\right)_{[\text{A}]=0} = K_1(2K_2 - K_1) \quad (9)$$

from which the following values were computed

$$K_2(25^\circ) = 13 \pm 2, K_2(50^\circ) = 9 \pm 2, K_2(75^\circ) = 4 \pm 2.5.$$

K_2 was also obtained from data at higher ligand concentrations by rearranging equation (8) and plotting a new function $G_2([\text{A}])$ versus the free ligand concentration

$$G_2([\text{A}]) = \frac{G_1([\text{A}]) - K_1(1 - \bar{n})}{[\text{A}]} = 2\beta_2\left(1 - \frac{\bar{n}}{2}\right) + \sum_{n=3}^{n=N} (n - \bar{n})\beta^n [\text{A}]^{n-2} \quad (10)$$

The intersection of the curve with the ordinate axis gives in this case: $2\beta_2 = 2K_1K_2$. Table 4 and Fig. 2 give some experiments at 50° with concentrations of free ligand from ~ 0.01 – 0.06 M. Unfortunately the colour of the solutions here made the titrations more uncertain. The value estimated for β_2 ($= 700$

Table 4. Data for estimation of K_2 in 1 M sodium perchlorate solution at 50° C.

No.	$C_{\text{Cr}} \times 10^3$	$C_{\text{SCN}^-} \times 10^3$	$[\text{SCN}^-] \times 10^3$	\bar{n}	$\frac{\bar{n}}{[\text{SCN}^-]}$	$G_2([\text{SCN}^-])$
1	27.58	29.75	13.8	0.576	42.7	1 190
2	30.59	39.68	18.1	0.710	39.2	1 170
3	34.38	49.60	22.2	0.797	35.9	1 050
4	46.05	89.4	39.6	1.082	27.3	816
5	49.12	99.2	43.1	1.142	26.5	820
6	52.07	109.2	48.2	1.172	24.3	726
7	57.74	128.8	60.3	1.186	19.7	517

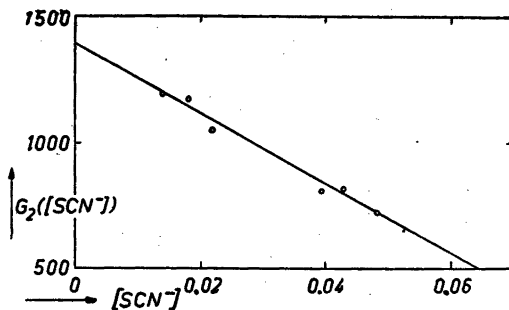


Fig. 2. Graphical estimation of $\beta_2 = K_1 K_2$ as the value of $\frac{1}{2} G_2$ ($[SCN^-]$) for $[SCN^-] = 0$.

± 50) indicates $K_2 = 11 \pm 1$ to be compared with the value 9 ± 2 obtained from Fig. 1.

From the temperature-dependence of K_1 and K_2 the following values for the heats of formation in kcal. were estimated:

$$-\Delta H_n = \frac{RT'T''}{T' - T''} \ln \frac{K'_n}{K''_n} \quad (T = \text{abs. temperature})$$

Temperature range	$-\Delta H_1$	$-\Delta H_2$
25°–50° C	1.4 ± 0.2	2 ± 2
50°–75° C	1.5 ± 0.5	8 ± 6

ESTIMATION OF VELOCITY CONSTANTS

The rate constant for the uptake of the 1st thiocyanate ion was determined by the same analysis-technique as used in the equilibrium experiments. Thermostated solutions containing the ions to react — and neutral salt, when this was used — were mixed in a 500 ml bottle also in the bath. Samples taken at different times were analyzed and the concentrations of free and total thiocyanate and total chromium determined. Only the first part of the reaction was followed where the reciprocal reaction and further transformations could be neglected, and the velocity constants were in all cases determined by means of the expression for a bimolecular reaction

$$k_1 = \frac{1}{t} \cdot \frac{2.303}{C_{Cr} - C_{SCN^-}} \log \frac{C_{Cr}[SCN^-]}{[Cr^{+++}]C_{SCN^-}} \quad (11)$$

Some preliminary experiments showed that the initial velocities were independent of the hydrogen ion concentration in the range 0.02–0.10 molar. Some experiments at different temperatures in 1 M NaClO₄, and in solutions without sodium perchlorate ($\mu \sim 0.1$) are given in Table 5. For each experiment is given the equilibrium value for the formation function \bar{n}_{eq} , and the data show that k_1 from the technique used can be determined with reasonable certainty from the very beginning of the reaction, where $\bar{n} \ll \bar{n}_{eq}$.

Table 5. Estimation of rate constants for uptake of the 1st thiocyanate ion.
 $C_{\text{HClO}_4} \sim 0.02$, $C_{\text{NaClO}_4} = 1.00$

Temp. °C	Time (min.)	$C_{\text{Cr}} \times 10^3$	$C_{\text{SCN}^-} \times 10^3$	$[\text{SCN}^-] \times 10^3$	$[\text{Cr}^{+++}] \times 10^3$	$k_1 \times 10^3$ ($\text{C}^{-1} \cdot \text{sec}^{-1}$)	n
25°	0	23.39	21.16	21.16	23.39		0
25°	1 260	23.39	21.16	20.95	23.18	0.00569	0.009
25°	2 880	23.39	21.16	20.56	22.79	0.00720	0.026
25°	4 320	23.39	21.16	20.32	22.55	0.00680	0.036
25°	5 760	23.39	21.16	20.18	22.41	0.00598	0.042
25°	8 640	23.39	21.16	19.92	22.15	0.00518	0.053
					Mean	0.0062 ± 0.0004	$0.494 \bar{n}_{\text{eq}}$
50°	0	20.46	19.17	19.17	20.46		0
50°	30	20.46	19.17	19.04	20.33	0.176	0.006
50°	60	20.46	19.17	18.92	20.21	0.175	0.012
50°	103	20.46	19.17	18.76	20.05	0.171	0.020
50°	189	20.46	19.17	18.52	19.81	0.152	0.032
					Mean	0.169 ± 0.006	$0.445 \bar{n}_{\text{eq}}$
75°	0	23.46	18.49	18.49	23.46		0
75°	11	23.46	18.49	17.73	22.69	2.79	0.032
75°	20	23.46	18.49	17.11	22.07	2.85	0.059
75°	40	23.46	18.49	15.97	20.93	2.77	0.108
75°	60	23.46	18.49	14.91	19.87	2.78	0.153
75°	90	23.46	18.49	13.87	18.83	2.55	0.197
					Mean	2.75 ± 0.05	$0.363 \bar{n}_{\text{eq}}$
Without sodium perchlorate ($\mu \sim 0.1$)							
50°	0	13.80	16.00	16.00	13.80		0
50°	27.5	13.80	16.00	15.92	13.72	(0.421)	0.005
50°	38.5	13.80	16.00	15.83	13.62	0.481	0.011
50°	78.5	13.80	16.00	15.56	13.35	0.508	0.028
50°	124	13.80	16.00	15.29	13.08	0.500	0.044
50°	178	13.80	16.00	15.01	12.80	0.482	0.062
50°	199	13.80	16.00	14.81	12.60	0.519	0.074
					Mean	0.498 ± 0.006	$\sim 0.64 \bar{n}_{\text{eq}}$
75°	0	13.50	12.28	12.28	13.50		0
75°	14.7	13.50	12.28	11.56	12.78	5.15	0.053
75°	28.5	13.50	12.28	10.85	12.07	5.59	0.106
75°	39.8	13.50	12.28	10.40	11.62	5.67	0.139
75°	49.6	13.50	12.28	9.94	11.16	5.54	0.173
75°	58.1	13.50	12.28	9.81	11.03	5.31	0.183
					Mean	5.5 ± 0.1	$\sim 0.43 \bar{n}_{\text{eq}}$

The values for the parameters in the Arrhenius equation E_1 and $\log Z_1$ in 1 M NaClO₄ and in solutions with $\mu \sim 0.1$ given in Table 1 are computed from the mean values for k_1 given in Table 5. The corresponding parameters for the reciprocal reaction E_{-1} and $\log Z_{-1}$ in 1 M NaClO₄ are computed by combination with the known values for the equilibrium constant K_1 in this medium using the relationships (3)–(6).

SPECTROPHOTOMETRIC ESTIMATION OF THE FREE THIOCYANATE AFTER ADDITION OF FERRIC SALT

In the presence of thiocyanate-richer complexes the silver nitrate titration fails, and N. Bjerrum³ has used in such cases colorimetric estimation of the free thiocyanate concentration after addition of ferric nitrate. The method is due to the very rapid formation and strong absorption of the iron(III) thiocyanate complexes. It has been developed here to an accurate spectrophotometric method, and used to study the velocity of the aquation of the hexathiocyanato complex.

The complexity constant of the monothiocyanato iron(III) complex is according to M. Møller¹⁰ as high as 197. Therefore even in rather dilute ferric salt solutions the main part of added thiocyanate is bound as monocomplex when $C_{\text{Fe}} \gg C_{\text{SCN}^-}$. The light absorption of the monocomplex is not much lower than that of the other thiocyanato iron(III) complexes. It has maximum absorption at $\sim 480 \text{ m}\mu$ ($\epsilon_{\text{FeSCN}^{++}}^{\text{max}} = 3800$). At $480 \text{ m}\mu$ the molar extinction coefficient of the hexathiocyanato chromium(III) is as low as 3.25 while the absorption of the ferric ions is negligible. We should therefore expect that the optical density D_{480} of such solutions eventually corrected for the absorption of added chromium salts should be very nearly proportional to the free thiocyanate concentration. That this is so is shown by the data given in Table 6. D_{480} (calc.) given in the last column of the table is calculated from the formulae:

$$D_{480} = 2220 C_{\text{NaSCN}} + 0.003 \quad (12)$$

$$D_{480} = 2500 C_{\text{NaSCN}} + 0.003 \quad (13)$$

for solutions with $C_{\text{NaClO}_4} = 1.00$ and without sodium perchlorate, respectively.

The experiments on the hydrolysis of the hexathiocyanato complex were made as follows: Thermostated 0.02 M HClO_4 (1 M as for NaClO_4 in one series) was added to a weighed amount of the very pure complex salt $\text{K}_3\text{Cr}(\text{SCN})_6 \cdot 4 \text{ H}_2\text{O}$ (see p. 924); the reaction time was reckoned from the moment of shaking. Samples taken from time to time by a Krogh syringe pipette were diluted 10.09 times in a volumetric flask and mixed with the adequate volumes of ferric nitrate and perchloric acid corresponding to the conditions in Table 6, and measured as quickly as possible in a Beckman DU spectrophotometer. To get reproducible results it was necessary to have not only the reaction flask but also the samples closed from light until measurement. The concentrations of free thiocyanate were computed by means of the relations (12) and

Table 6. Optical densities referring to a 1 cm cell at the wavelength $480 \text{ m}\mu$ for some ferric thiocyanate solutions at room temperature.

C_{NaClO_4}	C_{HClO_4}	$C_{\text{Fe}(\text{NO}_3)_3} \times 10^3$	$C_{\text{NaSCN}} \times 10^3$	$D_{480}(\text{exp.})$	$D_{480}(\text{calc.})$
	0.100	5.86	0.1501	0.378	0.378
	0.100	5.86	0.2996	0.752	0.752
	0.100	5.86	0.4990	1.246	1.250
1.00	0.100	5.86	0.1499	0.337	0.336
1.00	0.100	5.86	0.2994	0.668	0.668
1.00	0.100	5.86	0.4991	1.106	1.111

Table 7. Estimation of rate constants for the dissociation of the 1st thiocyanate ion from the hexathiocyanato complex.

Temp. °C	Time (min.)	C_{Cr} $\times 10^3$	D_{480}^{1cm} corr.	$[SCN^-]$ $\times 10^3$	$k_{-1} \times 10^5$ (sec ⁻¹)	\bar{n}
$C_{HClO_4} = 0.02, C_{NaClO_4} = 1.00$						
15.1	0	20.02	0			
15.1	29	20.02	0.035	0.145	(0.418)	5.99
15.1	125.5	20.02	0.158	0.704	0.477	5.97
15.1	181	20.02	0.241	1.082	0.511	5.95
15.1	243	20.02	0.305	1.372	0.487	5.93
15.1	333.5	20.02	0.438	1.977	0.520	5.90
				Mean	0.50 ± 0.01	
25°	0	19.96	0			
25°	39	19.96	0.213	0.954	2.10	5.95
25°	58.5	19.96	0.317	1.427	2.12	5.93
25°	81.5	19.96	0.447	2.018	2.18	5.90
25°	103	19.96	0.560	2.532	2.20	5.87
25°	127	19.96	0.680	3.077	2.19	5.85
25°	149	19.96	0.793	3.591	2.23	5.82
25°	175	19.96	0.914	4.140	2.22	5.79
25°	210.5	19.96	1.082	4.904	2.22	5.75
				Mean	2.18 ± 0.02	
Without sodium perchlorate ($\mu \sim 0.1$)						
15.1	0	20.06	0	0		
15.1	55.5	20.06	0.094	0.367	(0.555)	5.98
15.1	113.5	20.06	0.187	0.743	0.555	5.96
15.1	163.5	20.06	0.253	1.009	0.534	5.95
15.1	229.0	20.06	0.336	1.344	0.507	5.93
15.1	274.5	20.06	0.403	1.614	0.509	5.92
15.1	310.0	20.06	0.454	1.820	0.511	5.91
15.1	339.0	20.06	0.493	1.978	0.510	5.90
				Mean	0.521 ± 0.008	
25°	0	19.97	0	0		
25°	14.5	19.97	0.101	0.396	2.30	5.98
25°	48	19.97	0.326	1.304	2.35	5.94
25°	76	19.97	0.497	1.993	2.23	5.90
25°	101	19.97	0.648	2.603	2.31	5.87
25°	122	19.97	0.780	3.136	2.34	5.84
25°	140.5	19.97	0.886	3.564	2.33	5.82
25°	159	19.97	0.993	3.996	2.34	5.80
25°	180	19.97	1.107	4.456	2.34	5.78
				Mean	2.32 ± 0.01	

(13). The optical densities referring to a 1 cm cell — besides being corrected for the absorption of the chromium salt — were also corrected for the change occurring in the time interval between the sample being removed and measured. To this purpose an experiment was carried out with the ferric nitrate added to the reaction flask from the beginning. Ferric salt catalyzes the reaction to some extent — at the concentration used here ($C_{Fe(NO_3)_3} = 0.00586 M$) it increased the rate of the hydrolysis by about 70 %.

The hydrolysis reaction was only followed until $n \sim 5.8$, and the first order rate constants obtained from the expression

$$k_{-6} = - \frac{2.303}{t} \log \frac{C_{\text{Cr}} - [\text{SCN}^-]}{C_{\text{Cr}}} \quad (14)$$

are given in Table 7. Measurements were made at 15° and 25° C. The values for the parameters in the Arrhenius equation E_{-6} and $\log Z_{-6}$ in 1 *M* NaClO₄ and in solutions with $\mu \sim 0.1$ given in Table 1 are computed from the mean values for k_{-6} given in the table.

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