

## Thermochemical Studies of Hydrolytic Reactions

12. The Reactions of  $H^+$  and  $CrO_4^{2-}$  in 3 M  $Na(ClO_4)$ 

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The enthalpy and entropy changes of the reactions between  $H^+$  and the chromate ion,  $CrO_4^{2-}$ , have been determined by enthalpy titrations at 25°C in 3 M  $Na(ClO_4)$  medium. Using the equilibrium constants given by Sasaki<sup>1</sup> the following results were obtained.

Reaction	$\Delta H^\circ$ kJ mol <sup>-1</sup>	$\Delta S^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>
$H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^-$	$4.5 \pm 0.4$	$128 \pm 1$
$2H^+ + 2CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O$	$-11.2 \pm 0.2$	$230 \pm 1$

It is shown that the equilibrium constants for the reactions above could also be determined from the calorimetric titration data.

It is well known that on acidification of chromate ion,  $CrO_4^{2-}$ , the products  $HCrO_4^-$  and  $Cr_2O_7^{2-}$  are formed. The equilibrium constants,  $\beta_{11}$ , and  $\beta_{22}$ , for the reactions



in 3 M  $Na(ClO_4)$  at 25°C have been determined by Sasaki<sup>1</sup> from both spectrophotometric and emf data;  $\log \beta_{11} = 5.89 \pm 0.02$  and  $\log \beta_{22} = 13.98 \pm 0.04$  (the concentration unit is molarity throughout).

The aim of the present calorimetric investigation was the determination of the thermodynamic parameters for reactions (1) and (2), and also to find out how accurately equilibrium constants for a relatively simple system can be determined from enthalpy titration data.

## EXPERIMENTAL

Sodium chromate *p.a.* was recrystallized in an atmosphere of nitrogen. The stock solutions were standardized iodometrically and the result was checked by drying samples to constant weight and weighing as  $Na_2CrO_4$ .

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The calorimetric measurements were performed in two series, one with an automatically recording calorimeter as described by Johansson<sup>2</sup> and one with a calorimeter based on manual balancing of the Wheatstone bridge (null method) as described by Arnek and Kakolowicz.<sup>3</sup> The experiments were carried out as titrations in which successive additions of  $v$  ml of an acid solution T were made, from a thermostated buret, to  $V_0$  ml of a chromate solution S, in the calorimeter vessel. At the beginning of each experiment the solution S had the composition 3 M Na<sup>+</sup>,  $B_s$  M CrO<sub>4</sub><sup>2-</sup>,  $H_s$  M H<sup>+</sup> and  $(3 - 2B_s + H_s)$  M ClO<sub>4</sub><sup>-</sup>. The analytical H<sup>+</sup> excess in the solution S,  $\bar{H}_s$ , was initially zero in each experiment. The acid solution T contained  $H_T$  M HClO<sub>4</sub> and 3 M NaClO<sub>4</sub>. The values for  $B_s$ ,  $H_T$ , and  $V_0$  in the different experiments are given in Table 1.

Table 1. Survey of titrations.

Expt. No.	$B_s$ , mM	$H_T$ , mM	$V_0$ , ml
1 <sup>a</sup>	22.04	193.4	192.34
2 <sup>a</sup>	21.80	193.4	192.34
3 <sup>b</sup>	20.74	290.4	224.53
4 <sup>a</sup>	31.50	193.4	192.34
5 <sup>a</sup>	31.49	193.1	192.34
6 <sup>a</sup>	41.61	193.1	192.34
7 <sup>a</sup>	41.46	193.1	192.34
8 <sup>b</sup>	41.31	580.7	224.53
9 <sup>b</sup>	82.96	1161.0	224.53
10 <sup>b</sup>	124.4	1161.0	224.53

<sup>a</sup> Calorimeter described by Johansson.<sup>2</sup>

<sup>b</sup> Calorimeter described by Arnek and Kakolowicz.<sup>3</sup>

## RESULTS AND CALCULATIONS

The data from the calorimetric titrations have been treated by the generalized least squares computer program LETAGROP/KALLE<sup>4</sup> (calorimetric version of LETAGROP<sup>5,6</sup>). With this program the computer searches for the set of unknown parameters,  $k_i$ , which minimizes the error square sum,

$$U = \sum (Q_{\text{calc}} - Q_{\text{exp}})^2$$

where  $Q$  is the amount of heat evolved.

The result is a set of "best" parameters with their standard deviations and also the standard deviation in a single measurement,  $\sigma_Q$ .

The enthalpy changes for reactions (1) and (2),  $\Delta H^\circ_{11}$  and  $\Delta H^\circ_{22}$ , were first calculated using the values of the equilibrium constants  $\beta_{11}$  and  $\beta_{22}$  given by Sasaki.<sup>1</sup> The results obtained were (deviations correspond to  $\pm 3\sigma$ ):  $\Delta H^\circ_{11} = +4.52 \pm 0.38$  kJ mol<sup>-1</sup> and  $\Delta H^\circ_{22} = -11.21 \pm 0.16$  kJ mol<sup>-1</sup> and  $\sigma_Q = 0.17$  J. Correction was made for the reaction  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  ( $\Delta H^\circ = 54.6$  kJ mol<sup>-1</sup>,<sup>3</sup>  $\log K_w = -14.22$ <sup>8</sup> in 3 M NaClO<sub>4</sub>) which makes a small contribution to the amount of heat evolved at the first experimental point in each titration.

In a second calculation, both the enthalpies  $\Delta H^\circ_{11}$  and  $\Delta H^\circ_{22}$ , and the equilibrium constants,  $\beta_{11}$  and  $\beta_{22}$ , were treated as unknown parameters to

Table 2. Experimental data  $v$  (ml),  $Q_{\text{exp}}$  (J) and  $(Q_{\text{calc}} - Q_{\text{exp}})$  (J)

3.96	0.22	-0.37			
7.60	1.09	0.28	1.28	-0.29	-0.14
11.43	1.76	0.20	4.25	0.24	0.12
14.05	1.48	0.03	7.55	1.11	0.16
17.44	1.92	0.17	11.44	1.99	-0.01
21.60	2.85	-0.14	15.17	2.22	-0.04
Expt. 1			18.69	2.23	-0.01
			20.26	1.14	-0.12
2.00	-0.42	-0.08	22.12	0.93	0.00
4.00	0.79	-0.02	Expt. 2		
6.00	1.21	0.04			
8.00	1.55	-0.03	1.64	-0.06	-0.38
10.00	1.84	-0.14	4.64	0.60	-0.08
12.00	1.84	-0.01	8.15	1.44	-0.01
14.00	1.92	0.00	12.19	2.01	0.11
16.00	2.05	-0.11	16.03	2.13	0.16
18.00	0.29	-0.25	19.91	2.49	0.00
21.00	0.00	-0.08	23.92	2.78	-0.09
25.00	0.00	-0.10	27.55	2.56	-0.03
Expt. 3			29.65	1.53	-0.04
			32.60	1.18	-0.01
2.06	-0.10	-0.34	Expt. 4		
4.45	0.44	0.02			
8.17	1.52	-0.03	1.74	0.00	-0.43
12.23	1.83	0.31	4.60	0.58	-0.08
16.07	2.34	-0.05	8.45	1.63	-0.05
20.06	2.66	-0.10	12.38	2.20	-0.12
24.02	2.62	0.03	16.47	2.81	-0.36
27.77	2.71	-0.10	20.70	2.78	-0.05
30.17	1.78	-0.09	24.54	2.81	-0.21
33.98	0.80	-0.02	28.67	3.14	-0.26
Expt. 5			32.64	3.15	-0.30
			36.84	3.18	-0.12
1.99	-0.06	-0.37	40.66	3.07	-0.24
3.79	0.28	0.00	Expt. 6		
6.78	1.12	-0.07			
10.76	1.96	-0.01	2.00	0.29	0.05
14.73	2.33	-0.05	4.00	2.80	0.02
18.67	2.65	-0.18	6.00	3.43	0.17
22.75	2.89	-0.19	8.00	3.85	0.16
26.81	2.84	-0.04	10.00	4.14	0.13
30.77	2.93	-0.13	12.00	4.39	0.07
34.52	2.84	-0.12	14.00	4.60	0.00
38.62	3.22	-0.21	16.00	4.52	0.05
41.00	1.78	-0.04	18.00	0.25	-0.25
Expt. 7			21.00	-0.04	-0.08
			25.00	-0.13	-0.03
2.00	3.10	0.17	Expt. 8		
4.00	7.41	0.27			
6.00	8.74	0.10	3.00	6.90	0.07
8.00	9.16	0.28	6.00	12.64	0.25
10.00	9.79	0.04	10.00	19.20	0.08
12.00	10.08	0.02	14.00	20.59	-0.17
14.00	10.38	-0.07	18.00	21.13	-0.06
16.00	10.33	0.07	22.00	21.84	-0.34
18.00	0.67	-0.50	24.00	10.54	0.17
20.00	0.00	-0.13	28.00	0.13	-0.28
22.00	-0.04	-0.09	32.00	0.00	-0.32
Expt. 9			Expt. 10		

be determined. A minimum in the error square sum was found for the following values of the parameters:

$$\begin{array}{ll} \Delta H_{11}^{\circ} = 3.8 \pm 0.4 \text{ kJ mol}^{-1} & \Delta H_{22} = -11.2 \pm 0.3 \text{ kJ mol}^{-1} \\ \beta_{11} = (8.3 \pm 1.2) \times 10^5 \text{ M}^{-1} & \beta_{22} = (9.2 \pm 0.6) \times 10^{13} \text{ M}^{-3} \\ (\log \beta_{11} = 5.92 \pm 0.07) & (\log \beta_{22} = 13.96 \pm 0.03) \end{array}$$

It was thus possible to get a good estimate of the equilibrium constants  $\beta_{11}$  and  $\beta_{22}$ , from the calorimetric titration data only. The conditions for determining equilibrium constants from enthalpy titration data have been discussed in some detail in a previous paper.<sup>7</sup>

In Table 2 the experimental data ( $v, Q$ ) and the difference ( $Q_{\text{calc}} - Q_{\text{exp}}$ ) are given.

The thermochemical data for the reactions between  $\text{H}^+$  and  $\text{CrO}_4^{2-}$  are summarized below.

Reaction	$\Delta G^{\circ}$ , kJ mol <sup>-1</sup>	$\Delta H^{\circ}$ , kJ mol <sup>-1</sup>	$\Delta S^{\circ}$ , J K <sup>-1</sup> mol <sup>-1</sup>
(1) $\text{H}^+ + \text{CrO}_4^{2-} \rightleftharpoons \text{HCrO}_4^-$	$-33.6 \pm 0.1$	$4.5 \pm 0.4$	$128 \pm 1$
(2) $2\text{H}^+ + 2\text{CrO}_4^{2-} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	$-79.8 \pm 0.1$	$-11.2 \pm 0.2$	$230 \pm 1$
(3) $2\text{HCrO}_4^- \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	$-12.6 \pm 0.2$	$-20.3 \pm 0.5$	$-26 \pm 2$

For reaction (3) above a  $\Delta H$  value of  $-20 \pm 2$  kJ mol<sup>-1</sup> (at infinite dilution) has been reported by Hepler<sup>9</sup> (calorimetric method) and by Linge and Jones<sup>10</sup> (temperature dependence of spectrophotometric data).

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