Thermochemical Studies of Hydrolytic Reactions

10. The Reactions of H^+ and WO_4^{2-} in 3 M Na(ClO$_4$)

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The enthalpy and entropy changes of the reactions between H^+ and the wolframate ion, WO_4^{2-}, have been determined by enthalpy titrations at 25°C in 3 M Na(ClO$_4$) medium. Using the equilibrium constants given by Arnek and Sasaki [1,2] the following results were obtained (the limits correspond to 3 σ):

Reaction	$\Delta H°$, kcal	$\Delta S°$, e.u.
$6H^+ + 6WO_4^{2-} \rightleftharpoons W_6O_{21}^{6-} + 3H_2O$	-57.1 ± 1.0	49 ± 3
$7H^+ + 6WO_4^{2-} \rightleftharpoons HW_6O_{21}^{5-} + 3H_2O$	-62.5 ± 0.9	68 ± 3
$14H^+ + 12WO_4^{2-} \rightleftharpoons W_{12}O_{41}^{10-} + 7H_2O$	-126.9 ± 2.0	138 ± 7

In this Institute Sasaki [1] in 1961 studied the reaction between H^+ and the wolframate ion, WO_4^{2-}, at 25°C in 3 M Na(ClO$_4$) medium using a glass electrode. The main reaction was found to be

$$7H^+ + 6WO_4^{2-} = HW_6O_{21}^{5-} + 3H_2O$$

with the equilibrium constant log $\beta_{7,6} = 60.68 \pm 0.03$.

A recent recalculation [2] of the emf data by means of the computer program LETAGROPVRID [3,4] has shown that a slightly "better" explanation of the data is obtained assuming in addition to the species $HW_6O_{21}^{5-}$ also the species H_2WO_4, $W_6O_{21}^{6-}$ and $W_{12}O_{41}^{10-}$ with the following equilibrium constants

$$7H^+ + 6WO_4^{2-} = HW_6O_{21}^{5-} + 3H_2O \qquad \log \beta_{7,6} = 60.76 \pm 0.03$$
$$6H^+ + 6WO_4^{2-} = W_6O_{21}^{6-} + 3H_2O \qquad \log \beta_{6,6} = 52.46 \pm 0.10$$
$$14H^+ + 12WO_4^{2-} = W_{12}O_{41}^{10-} + 7H_2O \qquad \log \beta_{14,12} = 123.24 \pm 0.14$$
$$2H^+ + WO_4^{2-} = H_2WO_4 \qquad \log \beta_{2,1} = 11.3 \pm 0.1$$

The present calorimetric study was undertaken in order to obtain thermochemical data for the reactions above. In a previous communication [5] thermochemical data for the system $H^+ - MoO_4^{2-}$ have been reported.

EXPERIMENTAL

Sodium wolframate (Merck *p.a.*) was recrystallized once in an atmosphere of N_2. A stock solution, about 1 M Na_2WO_4, was prepared and kept in a polythene bottle. Sodium wolframate was analyzed by drying to constant weight at 150°C and weighing as Na_2WO_4.

The calorimeter has been described earlier.[6] The experiments were carried out as enthalpy titrations in which successive additions of v ml of an acid solution T were made, from a thermostated buret, to V_0 ml (224.53) of a wolframate solution S contained in the calorimeter vessel. At the beginning of each experiment the solution S had the composition 3 M Na^+, B_S M WO_4^{2-}, H_S M H^+ and $(3-2B_S+H_S)$ M ClO_4^-. The acid solution T contained H_T M $HClO_4$ and 3 M $NaClO_4$. The analytical H^+ excess in the solution S, H_S, was initially zero in each experiment. The values for B_S and H_T in the different experiments are given in Table 1. The range of Z (=average number of H^+

Table 1. Survey of experiments.

Expt. No.	1	2	3	4	5	6
B_S, mM	163.1	163.1	95.13	27.18	19.71	6.80
H_T, mM	871.1	580.7	580.7	290.4	290.4	72.6

bound per WO_4^{2-}) studied was $0<Z<7/6$. In this range the reactions were found to be instantaneous. Upon further acidification $(Z>7/6)$ slow reactions were encountered; there was a measureable heat effect even 10 min after an addition of acid from the buret into the calorimeter solution.

RESULTS AND CALCULATIONS

The reactions which have been studied can be written

$$pH^+ + qWO_4^{2-} = H_p(WO_4)_q^{(2q-p)-}$$
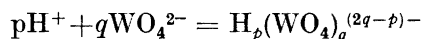
ΔH for this reaction may be called the relative molar enthalpy, $l_{p,q}$, of the species $H_p(WO_4)_q^{(2q-p)-}$ and its equilibrium constant will be called $\beta_{p,q}$.

After an addition of v ml of the acid buret solution T to the initial volume, V_0, of the wolframate solution S in the calorimeter vessel the excess enthalpy L in the calorimeter may be defined as

$$L = V\sum c_{p,q} \cdot l_{p,q}$$

where $c_{p,q}$ is the concentration of the species $H_p(WO_4)_q^{(2q-p)-}$ and $V=V_0+v$. If L' and V' are the excess enthalpy and volume before, and L'' and V'' the excess enthalpy and volume after an addition from the buret the heat evolved is

$$Q = L'-L''+(V''-V')l_T$$

where l_T (cal/l) is the excess enthalpy of solution T ("heat of dilution"). l_T was found from dilution experiments to be negligible.

The (Q,v) data from the enthalpy titrations were treated with the calorimetric version of the least squares computer program LETAGROPVRID.[3,4] With this program the computer searches for the set of unknown parameters

k_i which gives a minimum to the error square sum $U = \sum(Q_{calc} - Q_{exp})^2$. The unknown parameters to be determined in our case are the enthalpies $l_{p,q}$. The equilibrium constants $\beta_{p,q}$ were taken from the recalculation[2] of Sasaki's emf data.[1]

The results of the LETAGROPVRID calculations was a set of $l_{p,q}$ values with their standard deviations and also the standard deviation, σ_Q, in the measured quantity, Q.

Table 2. Results of LETAGROPVRID treatment. $\Delta H_{pq} \pm \sigma(\Delta H_{pq})$, U and σ_Q.

Calculation No.	I	II	III	IVa	IVb
$\Delta H_{7,6}$, kcal	-63.16 ± 0.09	-64.72 ± 0.20	-62.32 ± 0.32	-62.47 ± 0.38	-62.49 ± 0.31
$\Delta H_{14,12}$, kcal		-122.3 ± 0.5	-127.0 ± 0.6	-126.9 ± 0.7	-126.9 ± 0.66
$\Delta H_{6,6}$, kcal			-56.99 ± 0.31	-57.08 ± 0.38	-57.07 ± 0.34
$\Delta H_{2,1}$, kcal				-1 ± 24	0 n.v.[a]
$10^{-60} \cdot \beta_{7,6}$	6.4	5.63	5.14	5.82	5.82
$10^{-123} \cdot \beta_{14,12}$		1.48	1.65	1.73	1.73
$10^{-52} \cdot \beta_{6,6}$			2.88	2.88	2.88
$10^{-11} \cdot \beta_{2,1}$				1.98	1.98
U	1.68	0.93	0.46	0.46	0.46
σ_Q	0.144	0.108	0.076	0.077	0.076

[a] not varied
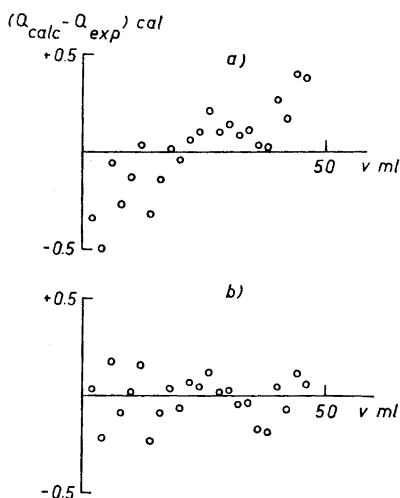

Fig. 1. Deviations $(Q_{calc} - Q_{exp})$ for $B_S = 0.1631$ M (experiment 1). a) calculated assuming only the species $HW_6O_{21}^{5-}$, b) calculated assuming the species $HW_6O_{21}^{5-}$, $W_6O_{21}^{6-}$ and $W_{12}O_{41}^{10-}$.
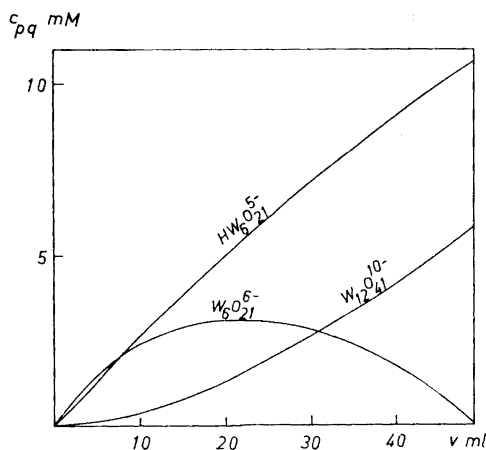
Fig. 2. Concentrations of $H_p(WO_4)_q^{(2q-p)-}$ during experiment 1 $(B_S = 0.1631$ M). The amount of H_2WO_4 is so small (<0.01 mM) as not to appear in the figure.

In Table 2 are given the results of the LETAGROPVRID calculations. Various combinations of the species with the (p,q) values (2,1), (6,6), (7,6) and (14,12) were tried. In calculation I in Table 2 only the species (7,6) was assumed to be present; with this assumption the heat data could not be satisfactorily interpreted which is illustrated in Fig. 1a. There is given, as an example, the quantity $(Q_{calc}-Q_{exp})$ *versus* v for experiment No. 1; $(Q_{calc}-Q_{exp})$ was calculated assuming only the species $HW_6O_{21}^{5-}$ with $\Delta H = -63.16$ kcal/mole. A systematic deviation in $(Q_{calc}-Q_{exp})$ is obviously present. Returning to Table 2 calculations II and III show that a considerable improvement (lower U and σ_Q values) is obtained by adding the species (6,6) and (14,12) to the (7,6) species. The systematic deviation in $(Q_{calc}-Q_{exp})$ then also disappears (Fig. 1b). An attempt to determine also $\Delta H_{2,1}$ failed (calc. IVa, Table 2). This was not unexpected as the amount of H_2WO_4 in the solutions is quite small (<0.02 mM). In calculation IVb $\Delta H_{2,1}$ was therefore put equal to zero and was not varied. Fig. 2 gives as an example the concentrations of the different species during experiment 1 ($B_S=163.1$ mM). It should be mentioned that no improvement of the fit between experimental and calculated values could be obtained by introducing small errors in the analytical wolframate concentration, B_S, as an adjustable parameter.

From the LETAGROPVRID calculations we thus obtained the following result (the deviations correspond to 3 σ):

$$\Delta H_{6,6} = -57.1 \pm 1.0 \text{ kcal/mole}$$
$$\Delta H_{7,6} = -62.5 \pm 0.9 \text{ kcal/mole}$$
$$\Delta H_{14,12} = -126.9 \pm 2.0 \text{ kcal/mole}$$

The standard deviation in Q, σ_Q, was 0.075 cal.

In Table 3 the experimental data (Q,v) and the difference $(Q_{calc}-Q_{exp})$ are given. No systematic deviations seem to be present which gives a certain support to the model proposed with the polyanions $W_6O_{21}^{6-}$, $HW_6O_{21}^{5-}$ and $W_{12}O_{41}^{10-}$.

INFLUENCE OF THE IONIC MEDIUM

The measurements hitherto described were all performed in the ionic medium 3 M $NaClO_4$ with $[Na^+]=3$ M. In order to investigate the possible effect of the medium on the enthalpy values, some experiments were performed without $NaClO_4$. Solutions of Na_2WO_4 in water with $[W(VI)]_{total}=0.16$, 0.1, 0.02 and 0.005 M were titrated with $HClO_4$. For $[W(VI)]_{total} \geq 0.1$ M the heat effects were the same within the limits of error as those obtained in 3 M $Na(ClO_4)$; the calculated enthalpies were $\Delta H_{6,6}=-58.4 \pm 1.5$ kcal/mole, $\Delta H_{7,6}=-60.6 \pm 1.6$ kcal/mole and $\Delta H_{14,12}=-134.9 \pm 5.9$ kcal/mole. For $[W(VI)]_{total} \leq 0.02$ M, however, the heat effects were significantly smaller than in 3 M $NaClO_4$; the value calculated for $\Delta H_{7,6}$ was -56.9 ± 0.8 kcal/mole (in this concentration range it was not possible to calculate $\Delta H_{6,6}$ and $\Delta H_{14,12}$). At these low ionic strengths it could no longer be assumed that the activity factors and partial molar enthalpies of the different wolframate species should be the same as in 3 M $NaClO_4$.

Table 3. Experimental data.

Values of v (ml), Q_{exp} (cal) and $(Q_{calc} - Q_{exp})$ (cal).

Expt. 1. $B_S = 163.1$ mM, $H_T = 871.1$ mM

2.00, 16.07, 0.03; 4.00, 16.22, -0.21; 6.00, 15.78, 0.18; 8.00, 15.99, -0.08; 10.00, 15.85,
0.02; 12.00, 15.68, 0.16; 14.00, 16.04, -0.23; 16.00, 15.86, -0.08; 18.00, 15.71, 0.04;
20.00, 15.78, -0.06; 22.00, 15.63, 0.07; 24.00, 15.63, 0.05; 26.00, 15.53, 0.12; 28.00, 15.61,
0.02; 30.00, 15.58, 0.03; 32.00, 15.63, -0.04; 34.00, 15.60, -0.03; 36.00, 15.71, -0.17;
38.00, 15.70, -0.18; 40.00, 15.45, 0.05; 42.00, 15.55, -0.07; 44.00, 15.32, 0.12; 46.00,
15.34, 0.07;

Expt. 2. $B_S = 163.1$ mM, $H_T = 580.7$ mM

2.00, 10.85, -0.10; 4.00, 10.70, 0.00; 6.00, 10.56, 0.11; 8.00, 10.61, 0.03; 10.00, 10.61,
0.01; 12.00, 10.50, 0.10; 14.00, 10.65, -0.07; 16.00, 10.53, 0.04; 18.00, 10.41, 0.14; 20.00,
10.52, 0.02; 22.00, 10.53, -0.01;

Expt. 3. $B_S = 95.13$ mM, $H_T = 580.7$ mM

2.00, 10.72, -0.06; 4.00, 10.64, -0.03; 6.00, 10.49, 0.09; 8.00, 10.57, -0.02; 10.00,
10.45, 0.08; 12.00, 10.56, -0.05; 14.00, 10.37, 0.12; 16.00, 10.53, -0.06; 18.00, 10.56,
-0.10; 20.00, 10.31, 0.13; 22.00, 10.50, -0.07; 24.00, 10.35, 0.07; 26.00, 10.48, -0.08;
28.00, 10.40, -0.01; 30.00 10.35, 0.03; 32.00, 10.35, 0.01; 34.00, 10.29, 0.06; 36.00, 10.31,
0.03;

Expt. 4. $B_S = 27.18$ mM, $H_T = 290.4$ mM

2.00, 5.25, 0.00; 4.00, 5.22, 0.02; 6.00, 5.22, 0.01; 8.00, 5.27, -0.05; 10.00, 5.18, 0.03;
12.00, 5.25, -0.04; 14.00, 5.26, -0.06; 16.00, 5.23, -0.04; 18.00, 5.23, -0.05; 20.00,
5.24, -0.07; 23.00, 7.69, 0.02;

Expt. 5. $B_S = 19.71$ mM, $H_T = 290.4$ mM

2.00, 5.25, -0.01; 4.00, 5.24, -0.02; 6.00, 5.22, -0.01; 8.00, 5.20, 0.00; 10.00, 5.13,
0.07; 12.00, 5.19, 0.00; 14.00, 5.16, 0.01; 16.00, 5.14, 0.01;

Expt. 6. $B_S = 6.80$ mM, $H_T = 72.6$ mM

2.00, 1.30, -0.01; 4.00, 1.31, -0.01; 6.00, 1.31, -0.01; 8.00, 1.32, -0.02; 10.00, 1.29,
0.01; 12.00, 1.32, -0.03; 14.00, 1.30, -0.01; 16.00, 1.31, -0.02; 18.00, 1.29, 0.00; 20.00,
1.29, -0.01; 22.00, 1.29, -0.03.

The results obtained in the present study do thus not seem to be restricted
to solutions containing 3 M $Na(ClO_4)$, but are also valid in solutions with
considerably lower ionic strength (at least about 0.3 M).

However, changes of the counter ion from Na^+ to, *e.g.*, Li^+ or K^+ could
be worthy of further study.

DISCUSSION

The thermochemical data for the reactions between H^+ and $WO_4{}^{2-}$ in
3 M $Na(ClO_4)$ at 25°C are summarized below. The zero superscript used with
ΔG, ΔH, and ΔS means that the standard states are hypothetical ideal one
molar solutions of the solutes in 3 M $Na(ClO_4)$ as the solvent.

Reaction	$\Delta G°$, kcal	$\Delta H°$, kcal	$\Delta S°$, e.u.
$6H^+ + 6WO_4^{2-} \rightleftharpoons W_6O_{21}^{6-} + 3H_2O$	-71.6 ± 0.14	-57.1 ± 1.0	49 ± 3
$7H^+ + 6WO_4^{2-} \rightleftharpoons HW_6O_{21}^{5-} + 3H_2O$	-82.9 ± 0.04	-62.5 ± 0.9	68 ± 3
$14H^+ + 12WO_4^{2-} \rightleftharpoons W_{12}O_{41}^{10-} + 7H_2O$	-168.1 ± 0.19	-126.9 ± 2.0	138 ± 7
$H^+ + W_6O_{21}^{6-} \rightleftharpoons HW_6O_{21}^{5-}$	-11.3 ± 0.2	-5.4 ± 1.3	20 ± 4
$2HW_6O_{21}^{5-} \rightleftharpoons W_{12}O_{41}^{10-} + H_2O$	-2.3 ± 0.2	-1.9 ± 2.4	1.3 ± 8

For a comparison we give the thermochemical data for the $H^+ - MoO_4^{2-}$ system earlier reported by Arnek and Szilard.[5]

Reaction	$\Delta G°$, kcal	$\Delta H°$, kcal	$\Delta S°$, e.u.
$8H^+ + 7MoO_4^{2-} \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O$	-78.77 ± 0.04	-56.0 ± 0.2	76 ± 1
$H^+ + Mo_7O_{24}^{6-} \rightleftharpoons HMo_7O_{24}^{5-}$	-6.00 ± 0.09	2.6 ± 0.3	29 ± 1
$H^+ + HMo_7O_{24}^{5-} \rightleftharpoons H_2Mo_7O_{24}^{4-}$	-4.83 ± 0.11	0.8 ± 0.5	19 ± 2
$H^+ + H_2Mo_7O_{24}^{4-} \rightleftharpoons H_3Mo_7O_{24}^{3-}$	-3.45 ± 0.13	-0.6 ± 1.3	10 ± 4

The characteristics of the reactions in which isopolywolframate and isopolymolybdate ions are formed are the large exothermity and the very favorable entropy changes of the reactions. The formation of water molecules in the condensation reactions may partly explain the large negative $\Delta H°$ values. The positive entropy changes are most likely due to the liberation of molecules of hydration water when the polyanions are formed.

It is unfortunate that it was not possible to obtain precise data for the mononuclear protonation of WO_4^{2-} and MoO_4^{2-} as it has been suggested that these reactions are the first steps in the condensation reactions.

Due to a more favorable enthalpy change the species $W_6O_{21}^{6-}$ takes up a proton more easily than $Mo_7O_{24}^{6-}$. $HW_6O_{21}^{5-}$ seems to be a very weak base which does not take up any further protons.

The condensation reaction $2HW_6O_{21}^{5-} \rightleftharpoons W_{12}O_{41}^{10-} + H_2O$ is accompanied by a very moderate entropy change ($\Delta S° = 1.3 \pm 8$ e.u.) which means that hydration effects here are of small importance.

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