Thermochemical Studies of Hydrolytic Reactions

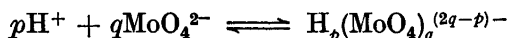## 9. The Reactions of H$^+$ and Molybdate Ions in 3 M Na(ClO$_4$)

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The enthalpy and entropy changes for the formation of HMoO$_4^-$ and the heptamolybdate ions (H$_x$Mo$_7$O$_{24}$)$^{(6-x)-}$, x = 0, 1, 2, 3, from H$^+$ and the molybdate ion MoO$_4^{2-}$ in 3 M Na(ClO$_4$) medium at 25°C have been determined by means of enthalpy titrations. Using the equilibrium constants given by Sasaki and Sillén[1] the following results were obtained (the limits correspond to 3σ):

Reaction	$\Delta H°$, kcal	$\Delta S°$, e.u.
H$^+$ + MoO$_4^{2-}$ $\rightleftharpoons$ HMoO$_4^-$	14 $\pm$ 7	65 $\pm$ 23
8H$^+$ + 7MoO$_4^{2-}$ $\rightleftharpoons$ Mo$_7$O$_{24}^{6-}$ + 4H$_2$O	-56.0 ± 0.2	76 $\pm$ 1
H$^+$ + Mo$_7$O$_{24}^{6-}$ $\rightleftharpoons$ HMo$_7$O$_{24}^{5-}$	2.6 $\pm$ 0.3	29 $\pm$ 1
H$^+$ + HMo$_7$O$_{24}^{5-}$ $\rightleftharpoons$ H$_2$Mo$_7$O$_{24}^{4-}$	0.8 $\pm$ 0.5	19 $\pm$ 2
H$^+$ + H$_2$Mo$_7$O$_{24}^{4-}$ $\rightleftharpoons$ H$_3$Mo$_7$O$_{24}^{3-}$	-0.6 ± 1.3	10 $\pm$ 4

The equilibria of molybdates in 3 M Na(ClO$_4$) medium have been studied at 25°C by emf titration by Sasaki and Sillén.[1] They found evidence for the formation of the mononuclear species MoO$_4^{2-}$, HMoO$_4^-$ and H$_2$MoO$_4$ and the heptanuclear species (H$_x$Mo$_7$O$_{24}$)$^{(6-x)-}$, x = 0, 1, 2, 3. They deduced the following equilibrium constants, $\beta_{p,q}$, for the reactions

$$p\text{H}^+ + q\text{MoO}_4^{2-} \rightleftharpoons \text{H}_p(\text{MoO}_4)_q^{(2q-p)-}$$

log $\beta_{1,1}$ = 3.89 $\pm$ 0.09; log $\beta_{2,1}$ = 7.50 $\pm$ 0.17;
log $\beta_{8,7}$ = 57.74 $\pm$ 0.03; log $\beta_{9,7}$ = 62.14 $\pm$ 0.06; log $\beta_{10,7}$ = 65.68 $\pm$ 0.06;
log $\beta_{11,7}$ = 68.21 $\pm$ 0.07

Evidence was also found for some large complex (*e.g.* log $\beta_{34,19}$ = 196.30 $\pm$ 0.26).

EXPERIMENTAL

Sodium molybdate (Mallinckrodt A.R.) was recrystallized three times from water in a platinum dish. The filtered crystals were kept under their own vapor pressure in an empty desiccator. An about 3 M anaqueous solution of the recrystallized salt did not

show any yellow colouring on acidification so it could be considered as practically silicate free. A stock solution (about 0.16 M) was made from the crystals and twice distilled water and kept in a polythene bottle in a closed desiccator above Ascarite. The content of molybdate in the stock solution was determined gravimetrically by 8-hydroxoquinoline.

The calorimeter has been earlier described.[2] 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 of a molybdate solution S contained in the calorimeter vessel. At the beginning of each titration the solution S had the composition 3 M Na^+, B_S M MoO_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 values for B, the total molybdate concentration, and H, the analytical excess hydrogen ion, in the different experiments are given in Table 1.

Table 1. Survey of experiments.

Expt. No.	1	2	3	4	5	6
B_S, M	0.1579	0.1607	0.1397	0.0824	0.0757	0.0413
B_T, M	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_S, M	0.01731	0.0000	0.1334	0.0000	0.08089	0.0000
H_T, M	0.9890	0.9890	0.9890	0.9890	0.9890	0.9890

V_0 was always 224.53 ml except in Expt. No. 1 where it was 228.53 ml. Fig. 1 shows as an example the cumulative heat effect, $\sum Q$ cal, during experiment No. 3. The initial and final $-\log h$ values were about 6 and 3.5.

RESULTS AND CALCULATIONS

The reactions which have been studied can be written

$$p\text{H}^+ + q\text{MoO}_4^{2-} = \text{H}_p(\text{MoO}_4)_q^{(2q-p)-}; \quad \Delta H = l_{p,q}$$
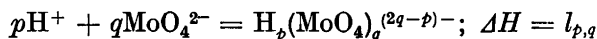
ΔH for this reaction may be called the relative molar enthalpy, $l_{p,q}$, of the complex $H_p(MoO_4)_q^{(2q-)p-}$ and its equilibrium constant will be called $\beta_{p,q}$. The values for the $\beta_{p,q}$ were taken from the emf work of Sasaki and Sillén.[1]

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

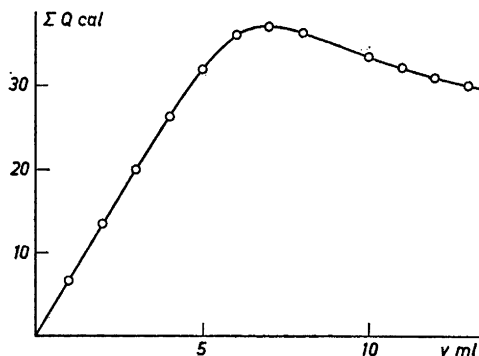$$L = V \sum c_{p,q} \cdot l_{p,q}$$

Fig. 1. The cumulative heat, $\sum Q$, as a function of the added volume v, in experiment No. 3.

where $c_{p,q}$ is the concentration of the species $H_p(MoO_4)_q^{(2q-p)-}$ 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 has been neglected in the following.

Pairs of (Q,v) values are obtained as a result of an enthalpy titration. To find the "best" values for the unknown $l_{p,q}$ we have used the calorimetric version of the least squares computer program LETAGROPVRID [3,4] on a CDC 3600 computer. With this program the computer searches for the set of values of the unknown parameters, k_i, which will minimize the error square sum

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

The input information used with the program in this case is: the equilibrium constants $\beta_{p,q}$ and estimates of the enthalpies $l_{p,q}$ (any value will do) (common to all the data); B_S, B_T, H_S, H_T, and V_0 (for each titration); v and Q (for each point in a titration). The output information is a set of $l_{p,q}$ values with their standard deviations and the standard deviation in the Q-measurements (σ_Q).

In the LETAGROPVRID calculations the enthalpies $l_{p,q}$ were treated as unknown independent parameters. Assuming small analytical errors in the determination of the molybdate concentrations, these errors were also treated as unknown. In fact, the molybdate concentrations could be determined more accurately from the enthalpy titrations than we could by analytical methods.

The LETAGROPVRID treatment gave the following result: $l_{1,1} = 14.2 \pm 2.3$ kcal; $l_{8,7} = -56.02 \pm 0.07$ kcal; $l_{9,7} = -53.47 \pm 0.08$ kcal $l_{10,7} = -52.67 \pm 0.13$ kcal; $l_{11,7} = -53.23 \pm 0.42$ kcal.

An early attempt to determine also $l_{2,1}$ gave the result $l_{2,1} = 32 \pm 22$ kcal/mole; the complex H_2MoO_4 was therefore left out ($\beta_{2,1}$ was put equal to 0) in the subsequent calculations.

The standard deviation, σ_Q, in the Q-measurements was 0.12 cal. The limits given are the standard deviations calculated by LETAGROPVRID.

In Table 2 the experimental data (v,Q) and the difference $(Q_{calc} - Q_{exp})$ are given. For each titration the molybdate concentration, B_S, with its deviation (3σ) obtained from the LETAGROPVRID treatment is also given.

Table 2. Experimental data.

Values of v [ml], Q_{exp}[cal], $(Q_{calc} - Q_{exp})$[cal]
Expt. 1. $B_S = 157.86 \pm 0.14$ mM, $H_S = 17.31$ mM
2.00, 13.59, 0.20; 4.00, 13.90, −0.10; 6.00, 13.93, −0.12; 8.00, 13.57, 0.24; 10.00, 13.98, −0.17; 12.00, 13.87, −0.06; 14.00, 13.68, 0.12; 16.00, 13.71, 0.11; 18.00, 13.66, 0.16; 20.00, 13.81, −0.02; 22.00, 13.76, 0.04; 24.00, 13.72, 0.04; 26.00, 13.65, 0.10; 28.00, 13.64, 0.08; 30.00, 13.73, −0.09; 32.00, 13.66, −0.08; 34.00, 13.33, −0.06; 36.00, 12.55, −0.12; 38.00, 8.43, −0.01; 41.00, −1.60, −0.01;
Expt. 2. $B_S = 160.69 \pm 0.01$ mM, $H_S = 0.00$ mM
2.00, 13.15, −0.04; 4.00, 13.78, −0.02; 6.00, 13.62, 0.17; 8.00, 13.73, 0.07; 10.00, 14.03, −0.22; 12.00, 13.55, 0.26; 14.00, 13.95, −0.14; 16.00, 13.61, 0.20; 18.00, 13.80, 0.01;

20.00, 13.55, 0.25; 22.00, 13.83, -0.01; 24.00, 13.54, 0.25; 26.00, 13.84, -0.04; 28.00, 13.82, -0.06; 30.00, 13.68, 0.07; 32.00, 13.56, 0.16; 34.00, 13.59, 0.06; 36.00, 13.80, -0.25; 38.00, 13.33, -0.05; 40.00, 12.61, -0.17; 42.00, 8.41, 0.04; 44.00, -0.14, -0.06;

Expt. 3. $B_S = 139.72 \pm 0.05$ mM, $H_S = 133.4$ mM
1.00, 6.64, 0.13; 2.00, 6.81, -0.13; 3.00, 6.55, 0.03; 4.00, 6.32, -0.05; 5.00, 5.85, -0.15; 6.00, 3.91, 0.11; 7.00, 1.06, 0.12; 8.00, -0.80, -0.05; 10.00, -2.82, -0.09; 11.00, -1.37, -0.02; 12.00, -1.10, -0.10; 13.00, -0.89, -0.02;

Expt. 4. $B_S = 82.4 \pm 0.2$ mM, $H_S = 0.00$ mM
2.00, 13.26, -0.09; 4.00, 13.76, 0.01; 5.98, 13.97, -0.32; 8.00, 13.95, -0.02; 10.00, 13.76, 0.04; 12.00, 13.75, 0.02; 14.00, 13.88, -0.12; 16.00, 13.59, 0.08; 18.00, 13.68, -0.13; 20.00, 12.97, -0.01; 22.00, 7.67, 0.09; 23.00, -0.77, 0.15; 24.00, -1.37, 0.01; 25.03, -1.21, 0.08;

Expt. 5. $B_S = 75.67 \pm 0.01$ mM, $H_S = 80.89$ mM
1.00, 5.44, -0.08; 1.90, 2.26, 0.05; 3.00, -0.60, 0.06; 4.00, -1.33, -0.03; 5.00, -1.13, 0.03; 6.00, -0.68, -0.05; 7.00, -0.26, 0.00;

Expt. 6. $B_S = 41.33 \pm 0.03$ mM, $H_S = 0.00$ mM
1.00, 6.20, 0.15; 2.00, 7.01, -0.15; 4.00, 13.84, -0.08; 6.00, 13.70, 0.06; 8.00, 13.87, -0.21; 10.00, 13.09, -0.09; 11.00, 4.03, -0.11; 12.00, -0.62, 0.11; 13.00, -0.92, 0.11.


DISCUSSION

The thermochemical data for the reactions between H^+ and MoO_4^{2-} in 3 M $Na(ClO_4)$ at 25°C are given 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.
1) $H^+ + MoO_4^{2-} = HMoO_4^-$	-5.31 ± 0.12	14 ± 7	65 ± 23
2) $8H^+ + 7MoO_4^{2-} = Mo_7O_{24}^{6-} + 4H_2O$	-78.77 ± 0.04	-56.0 ± 0.2	76 ± 1
3) $H^+ + Mo_7O_{24}^{6-} = HMo_7O_{24}^{5-}$	-6.00 ± 0.09	2.6 ± 0.3	29 ± 1
4) $H^+ + HMo_7O_{24}^{5-} = H_2Mo_7O_{24}^{4-}$	-4.83 ± 0.11	0.8 ± 0.5	19 ± 2
5) $H^+ + H_2Mo_7O_{24}^{4-} = H_3Mo_7O_{24}^{3-}$	-3.45 ± 0.13	-0.6 ± 1.3	10 ± 4

The $\Delta H°$ value for the first protonation of the molybdate ion MoO_4^{2-}, 14.2 kcal, must be regarded as very uncertain. This is due to the fact that the complex $HMoO_4^-$ gives a detectable contribution to the measured heat effect only in three experimental points (the first point in experiments Nos. 2, 4, and 6).

The high evolution of heat on the formation of the heptamolybdate ion $Mo_7O_{24}^{6-}$ (reaction 2) may be commented upon a little. The thermochemical data for the reaction 2) above may be compared with the data for the reaction (in 3 M $NaClO_4$)

	$\Delta G°$, kcal [5]	$\Delta H°$, kcal [2]	$\Delta S°$, e.u.
$4H^+ + 4OH^- \rightleftharpoons 4H_2O$	-77.6	-52.2	84
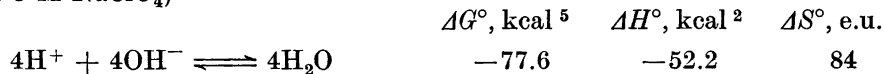
It seems not unreasonable to suggest that the main part of the enthalpy and entropy effect associated with reaction 2) can be explained by the formation of the four water molecules.

The stepwise protonations of $Mo_7O_{24}^{6-}$ to give $HMo_7O_{24}^{5-}$, $H_2Mo_9O_{24}^{4-}$ and $H_3Mo_7O_{24}^{3-}$ are greatly favoured by the entropy terms. The trend in

the values for $\Delta H°$ and $\Delta S°$ going from reaction 3) to 4) and 5) probably reflects the decreasing hydration of the heptamolybdate ions as they become protonated and their charge partly neutralised.

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