Thermochemical Study of Reduction and Oxidation Reactions of Molybdovanadophosphoric Heteropolyacids in Aqueous Solutions

E. G. Zhizhina,*[a] V. F. Odyakov,[a] and K. I. Matveev[a]

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Differential enthalpies of reduction, $-\Delta_r H_{4j}$, have been found at 343 K for 0.2 m aqueous heteropolyacids $H_{3+x}PV_xMo_{12-x}O_{40}$ (HPA-x, where $1 \leq x \leq 6$) and their salts by hydrazine hydrate (HH). The $-\Delta_r H_{4j}$ values depend on x and m, where $m = [V^{IV}]/[\text{HPA-x}]$. At $m \approx 0$, the initial $-\Delta_r H_{4j}$ value is 436 ± 14 kJ mol^{-1} HH for all HPA-x. For HPA-x with $3 \leq x \leq 6$, the curves $-\Delta_r H_{4j} = f(m_j)$ have maxima associated with formation and reduction of the outer-sphere cation $V^VV^{IV}O_3^{3+}$. A similar maximum is observed on reduction of 0.1 M VO_2ClO_4 in 4 m $HClO_4$. No maxima are observed for the reduction of HPA-1, HPA-2, and salts of HPA-3. For HPA-3 salts, $-\Delta_r H_{4j} = f(m_j)$ depends primarily on the pH of the salt solution, rather than on the nature of the cation. Reduction and oxidation of HPA-x and their salts are reversible reactions. In HPA-x solutions, VO_2^+ in the outer sphere is reduced first, and V^V in the inner coordination sphere of the heteropoly anion is reduced next. Differential enthalpies for the oxidation of the reduced HPA-x by dioxygen ($-\Delta_r H_{2j}$) have been calculated. The sequence of the oxidation of different V^{IV} forms in the reduced H_mHPA-x solutions is the reverse of that for the reduction of the V^V forms in the initial HPA-x solutions.

Introduction

The aqueous solutions of heteropolyacids $H_{3+x}PV_xMo_{12-x}O_{40}$ (HPA-x, $1 \leq x \leq 6$) of the Keggin structure and their acidic salts with cations such as $M_bH_{3+x-bz}PV_xMo_{12-x}O_{40}$ (where z is the cation charge and b is the number of cation atoms), are widely used as homogeneous oxidation catalysts, for example, in reactions[1][2] such as the oxidation of ethylene to acetaldehyde,[3] C_3-C_8 olefins to ketones,[4][5] CO to CO_2,[6] and H_2S to sulfur.[7] Substituted phenols and hydroxynaphthalenes are selectively oxidized in the presence of these catalysts to p-quinones.[8][9] The compounds HPA-x are very promising catalysts for oxidation of many other substrates.

In oxidation catalysis, the ability of HPA-x to perform reversible reductions[10][11] is used. Thus, the oxidation of substrates (Su) by reaction according to Equation 1 is followed by the reduction of HPA-x to H_mHPA-x, where $H_m\text{HPA-}x = H_{3+x+m}PV_m^{IV}V^V_{x-m}Mo_{12-x}O_{40}$ [where m is the number of vanadium(IV) atoms]. The reduced forms, H_mHPA-x, are oxidized further by dioxygen (reaction according to Equation 2) regenerating the initial HPA-x forms. Thus, reduction and oxidation of HPA-x/H_mHPA-x correspond to the valence transition $V^V \rightarrow V^{IV}$ and back. The substrate oxidation is, therefore, a combined catalytic process.

$$\text{Su} + H_2O + {}^2/_m\ \text{HPA-}x \rightarrow \text{SuO} + {}^2/_m\ H_m\text{HPA-}x \quad (1)$$

$$^4/_m\ H_m\text{HPA-}x + O_2 \rightarrow {}^4/_m\ \text{HPA-}x + 2\ H_2O \quad (2)$$

$$2\ \text{Su} + O_2 \xrightarrow{\text{HPA-}x} 2\ \text{SuO} \quad (3)$$

It is very important to exclude any direct contact between the oxidized substrate and dioxygen, as the latter can form explosive mixtures with gaseous substrates (e.g. C_2H_4). This precaution is also necessary if dioxygen initiates some side reactions. In this case, stages (1) and (2) must be performed in separate reactors.[12]

It is necessary to know the heat effects and enthalpies of each stage, such as $\Delta_rH_1 = -q_1/n_{Su}$ and $\Delta_rH_2 = -q_2/n_{O_2}$ where n is the number of moles and the heats, q and q_2 are the enthalpies of reactions (1) and (2), Δ_rH_1 and Δ_rH_2, respectively.

The enthalpy of reaction (3) is readily found as the difference between standard (tabled) enthalpies of the product and the substrate formation (SuO and Su): $\Delta_rH_3 = \Delta_fH_{SuO} - \Delta_fH_{Su}$. However, the enthalpies of stages (1) and (2) are still unknown, since there is no reliable information in the literature on the enthalpies of HPA-x reduction and oxidation.

Reaction (2) is common for oxidation processes of type (3). However, direct measurements of its heat effects are hindered, because its rate changes by three powers of ten.[13] To calculate the heat effects of reactions (1) and (2), the difference of enthalpies $\Delta_fH_{H_m\text{HPA-}x} - \Delta_fH_{\text{HPA-}x}$ must be known; this difference can be found experimentally using a model reaction. The most reliable and accurate data for Δ_rH_2 were obtained indirectly by measuring the heats of reaction for the oxidation of hydrazine hydrate (HH) by heteropolyacid to release gaseous N_2,[14] that is, heats q_4 of reaction (4).

$$N_2H_4\cdot H_2O + {}^4/_m\ \text{HPA-}x \rightarrow N_2\uparrow + {}^4/_m H_m\text{HPA-}x + H_2O \quad (4)$$

If Δ_rH_4 for reaction (4) and Δ_rH_5 for reaction (5) are known, one can readily calculate Δ_rH_2 by Equation (6).

$$N_2H_4\cdot H_2O + O_2 \rightarrow N_2 + 3\ H_2O \quad (5)$$

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[a] Boreskov Institute of Catalysis,
Prospekt Akademika Lavrentieva 5, Novosibirsk, 630090, Russia
Fax: (internat.) + 7-3832/343056
E-mail: matv@catalysis.nsk.su

$$\Delta_rH_2 = \Delta_rH_5 - \Delta_rH_4 \quad (6)$$

The enthalpies of reactions (1) and (2) for various HPA-x compounds are also significant for steering of catalytic activity of HPA-x ions in these reactions.

The initial (oxidized) forms of HPA-x dissociate reversibly eliminating cation VO_2^+ by reaction (7) due to the acidity of HPA-x itself.[15][16] In turn, the reduced H_mHPA-x forms ($m = x$) eliminate the cation VO^{2+} even more easily by reaction (8),[17][18] resulting in an increase of pH in the course of reduction of HPA-x solutions.[9]

$$(13-x)PV_xMo_{12-x}O_{40}^{(3+x)-} + 27\,H^+ \overset{K_{ox}}{\rightleftharpoons} (12-x)PV_{x-1}Mo_{13-x}O_{40}^{(2+x)-} + 12\,VO_2^+ + H_3PO_4 + 12\,H_2O \quad (7)$$

$$(13-m)PV^{IV}{}_mMo_{12-m}O_{40}^{(3+2m)-} + 51\,H^+ \overset{K_{rel}}{\rightleftharpoons} (12-m)PV^{IV}{}_{m-1}Mo_{13-m}O_{40}^{(1+2m)-} + 12\,VO^{2+} + H_3PO_4 + 24\,H_2O \quad (8)$$

Therefore, the enthalpies Δ_rH_1,and Δ_rH_4 depend on $m = [V^{IV}]/[HPA\text{-}x]$, which is the degree of HPA-x reduction.[17] They also depend on the solvent nature which influences the degree of HPA-x or H_mHPA-x dissociation in reactions (7) and (8).

The only thermochemical study of reaction (4)[14] was performed using HPA-x solutions with a high concentration of SO_4^{2-} anions, which essentially affected the results. The SO_4^{2-} anion forms complexes with both VO_2^+[19] and VO^{2+}.[20][21] Enthalpies of formation for the sulfate complexes are different, and they depend differently on solution pH. In turn, the pH of HPA-x solutions depends on the degree of HPA-x reduction (see Figure 5 in ref.[9]). These features enhance the complexity of the composition of HPA-x solutions,[14] and somehow affect the enthalpy values. In addition, some heat losses caused by scattering were not taken into account,[14] because the heats were measured at room temperature (299 K), when reaction (4) proceeded very slowly (up to 80 min).

Results and Discussion

Here and later, we use index j for the interpolated values of m_j and Δ_rH_{4j}. The same values without an index refer to the reference data.

Reduction of VO_2ClO_4 Solutions by Hydrazine Hydrate

Solutions of VO_2ClO_4 (0.1 M) in $HClO_4$ have a simple composition. They are reduced by hydrazine hydrate (HH) by reaction (9).

$$4\,VO_2^+\,(aq.) + N_2H_4\,(aq.) + 4\,H^+\,(aq.) \rightarrow 4\,VO^{2+}\,(aq.) + N_2\uparrow + 4\,H_2O \quad (9)$$

The calculation of the enthalpy for reaction (9) from the enthalpies of formation Δ_fH for each component (data from ref.[22]) gives: $-\Delta_rH_9 = 524.8$ kJ mol^{-1} HH. However, experimental $-\Delta_rH_{9j}$ values were often not constant, and changed with α_j, where $\alpha = [VO^{2+}]/([VO^{2+}] + [VO_2^+])$ is the fraction of vanadium reduced to VO^{2+} (aq.) (Figure 1).

When $[HClO_4] = 1$ M, $-\Delta_rH_9$ does not depend on α and is equal to 435 ± 6 kJ mol^{-1} HH (Figure 1, curve 1). When $[HClO_4] = 4$ M, there is a sharp maximum $-\Delta_rH_{9j} = f(\alpha_j)$ (Figure 1, curve 2), which reaches ca. 660 kJ mol^{-1} HH at $[VO_2^+] \approx [VO^{2+}]$. We attribute this maximum to formation of a cation with mixed valences of vanadium by reaction (10).

$$VO_2^+(aq.) + VO^{2+}(aq.) \rightleftharpoons V^VV^{IV}O_3^{3+}\,(aq.) \quad (10)$$

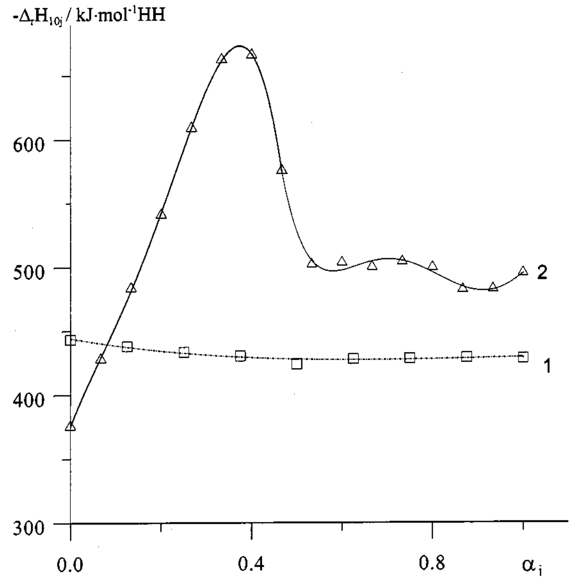

Figure 1. Differential enthalpies for reaction (9) vs. fraction of vanadium reduced to VO^{2+} (aq.) for 0.1 M solutions of VO_2ClO_4: 1: $[HClO_4] = 1$ M; 2: $[HClO_4] = 4$ M

The formation of such a cation was also observed by spectrophotometry in ≥ 3 M H_2SO_4 or $HClO_4$,[23][24] but not in 1 M $HClO_4$.[24] The composition of this cation with mixed valences of vanadium is likely to be $V^V{}_2V^{IV}O_4^{6+}$ rather than $V^VV^{IV}O_3^{3+}$.[23][24] Such a composition is more consistent with the influence of acidity on $V^V{}_2V^{IV}O_4^{6+}$ formation, and the position of the maximum in curve 2 (Figure 1).

$$2\,VO_2^+\,(aq.) + VO^{2+}\,(aq.) + 2\,H^+ \rightleftharpoons V^V{}_2\,V^{IV}O_4^{6+}\,(aq.) + H_2O \quad (10a)$$

Reduction of Aqueous $H_{3+x}PV_xMo_{12-x}O_{40}$ Solutions by Hydrazine Hydrate

For $x = 1$, ^{31}P- and ^{51}V-NMR spectra of HPA-1 solution show the presence of only one heteropoly anion $PVMo_{11}O_{40}^{4-}$.[25] For $x > 1$, these spectra show that solutions of average composition $PV_xMo_{12-x}O_{40}^{(3+x)-}$ actually contain the complex equilibrium mixtures of different individual heteropoly anions $PV_yMo_{12-y}O_{40}^{(3+y)-}$, where $y = x$, $x \pm 1$, $x \pm 2$, etc.,[25][26] including their isomers.[27] These solutions also contain equilibrium concentrations of VO_2^+ cation, and $H_zPO_4^{(3-z)-}$ anions.[21] The heat evolution coincided at times with the nitrogen liberation. The absence of any heat effects after complete dinitrogen liberation indicates that the equilibration between different heteropoly anions is faster than any interaction of these anions with HH.

The cations VO_2^+ in HPA-x solutions are considered to exist as outer-sphere complexes with $PV_yMo_{12-y}O_{40}^{(3+y)-}$ anions (see below). According to ^{51}V-NMR spectroscopy,[28] an outer-sphere complex of VO_2^+ and HPA-2 is formed from HPA-2 and $Na_6V_{10}O_{28}$ in a of solution water + acetic acid. Thus, reduction of HPA-x solutions in reaction (4) is more complicated than that of VO_2^+ (aq.) in reaction (9).

The relationships $-\Delta_rH_{4j} = f(m_j)$ for reduction of different HPA-x or their salts depend on the number x. On reduction of HPA-1 and HPA-2, $-\Delta_rH_{4j}$ values decrease gradually with an increase of m_j (Figure 2, curves 1 and 2). This decrease is especially sharp when m_j is close to x. The initial $-\Delta_rH_{4j}$ values (at $m_j \leq 0.5$) are 431 ± 11, and 440 ± 14 kJ mol^{-1} HH for HPA-1 and HPA-2, respectively. Note that these values are very close to $-\Delta_rH_{9j} = 435 \pm 6$ kJ mol^{-1} HH for reduction of 0.1 M VO_2ClO_4 in 1 M $HClO_4$. At $m_j > x$, HPA-1 reduces further, indicating a valence transition of Mo^{VI} to Mo^{V} (see Figure 2, curve 1) . Such an over-reduction of HPA-1 was also observed by potentiometry.[18][29]

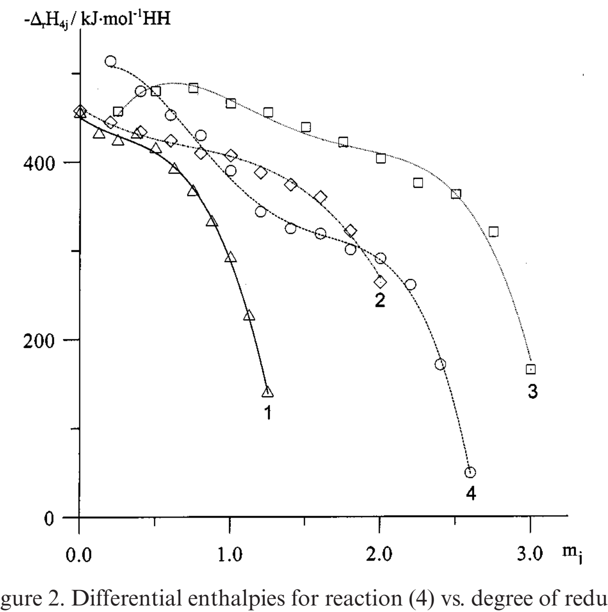

Figure 2. Differential enthalpies for reaction (4) vs. degree of reduction of various HPA-x and salts of HPA-3 in 0.2 M aqueous solutions: 1: $H_4PVMo_{11}O_{40}$; 2: $H_5PV_2Mo_{10}O_{40}$; 3: $H_6PV_3Mo_9O_{40}$; 4: $MgH_4PV_3Mo_9O_{40}$, $Na_2H_4PV_3Mo_9O_{40}$, and $K_2H_4PV_3Mo_9O_{40}$

For HPA-x with $x \geq 3$, the relationships $-\Delta_rH_{4j} = f(m_j)$ have a maximum (Figures 2 and 3), when $-\Delta_rH_{4j}$ values increase slightly at first (as m_j values are low) and then decrease. The higher the value of x (the number of vanadium atoms in HPA-x), the greater the shift of maximum $-\Delta_rH_{4j}$ to the region of high m_j values. Thus, the maximum occurs at $m_j \approx 0.65$ for HPA-3 (Figure 2, curve 3), and at $m_j \approx 1.2$ for HPA-4 and HPA-6 (Figure 3). For the latter solutions, there is a region of m_j after the maximum of $-\Delta_rH_{4j}$, where $-\Delta_rH_{4j}$ values practically do not change and reach 300 ± 7 kJ mol^{-1} HH. This region with a roughly constant $-\Delta_rH_{4j}$ occurs at ca. $2.5 \leq m_j \leq 3.5$, and ca. $3 \leq m_j \leq 5.8$ for HPA-4, and HPA-6, respectively.

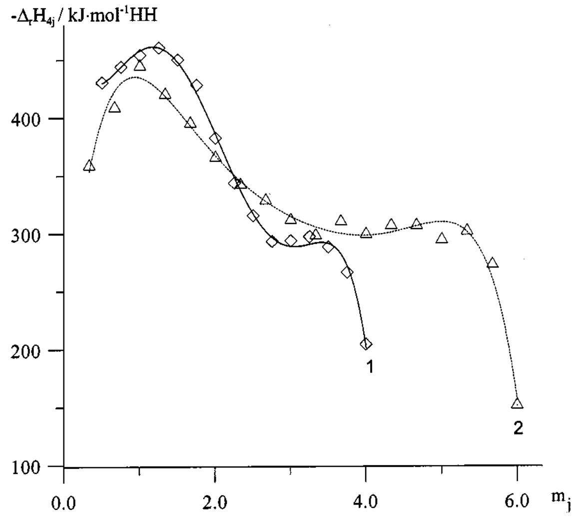

Figure 3. Differential enthalpies for reaction (4) vs. degree of reduction of HPA-x in 0.2 M aqueous solutions: 1: $H_7PV_4Mo_8O_{40}$; 2: $H_9PV_6Mo_6O_{40}$

For HPA-x solutions regenerated with dioxygen or H_2O_2, $-\Delta_rH_{4j} = f(m_j)$ relationships agree with those for fresh HPA-x solutions. Therefore, the composition and properties of HPA-x solutions are completely reversible.

For 0.2 M solutions of salts $M^I_2H_4PMo_9V_3O_{40}$ with cation $M^I = Na^+$, K^+, or 1/2 Mg^{2+}, the relationships $-\Delta_rH_{4j} = f(m_j)$ do not depend on the cation nature (Figure 2, curve 4). The $-\Delta_rH_{4j}$ values for these salts are lower than for HPA-3 itself (Figure 2, curve 3). This difference is associated with higher values of $pH_j = \varphi(m_j)$ for HPA-3 salts as compared with HPA-3 itself. Thus, the pH_0 of 0.2 M HPA-3 is ca. 0.4, whereas the pH_0 of each 0.2 M twice-substituted salt of HPA-3 is ca. 0.6.

Table 1. Dependence of m_j and Δ_rH_{4j} on the pH_j value for 0.2 M solutions of HPA-3 and its magnesium salt; index a refers to the acid, index s refers to the salt

0.2 M solution	pH_j	Interpolated values m_{ja} or m_{js}	$-\Delta_rH_{4j}$ [kJ mol^{-1} HH]
$H_6PMo_9V_3O_{40}$	0.8	1.65	429
$MgH_4PMo_9V_3O_{40}$		0.75	435
$H_6PMo_9V_3O_{40}$	1.0	2.14	391
$MgH_4PMo_9V_3O_{40}$		1.06	381

As m increases, the pH values of different HPA-x or their salts solutions increase too.[9] That is, pH = $\varphi(m)$. We chose m_{ja} values for HPA-3 itself, and m_{js} values for HPA-3 salts in order to obtain the same pH_j values for their solutions (see Table 1). It is proved that $-\Delta_r H_{4j}$ values are very similar, when pH_j are identical. Thus, relationships $-\Delta_r H_{4j} = f(m_j)$ for HPA-x salts depend primarily on the pH of HPA-x salt solution rather than on the nature of cation M.

For partially reduced 0.2 M solutions of HPA-x, the pH values are limited within $0.4 \leq pH \leq 1.5$.[9] At these pH values, cation VO_2^+ (aq.) is readily hydrolyzed to acid $H_2V_{12}O_{31} \cdot xH_2O$,[30] whose solubility is 0.047 g at V L^{-1} in 0.2 M $HClO_4$.[31] According to ^{51}V-NMR spectroscopy, the equilibrium concentration of VO_2^+ is about 0.1 M, 0.16 M, and 0.4 M in 0.2 M solution of HPA-3, HPA-4, and HPA-6, respectively.[26] Such a concentration is much higher than the equilibrium concentration of VO_2^+ in the absence of heteropoly anions and other complexing agents. Therefore, VO_2^+ is not free in HPA-x solutions. It evidently forms outer-sphere complexes with heteropoly anions. Thus, the solvated large heteropoly anion (> 1.3 nm in size[32]) is considered as an acidic particle with weakly bound less acidic cations VO_2^+ and VO^{2+}. (Their sizes do not exceed 0.3 nm.[33])

Reaction (10) between cations VO_2^+ and VO^{2+} can proceed either in 4 M $HClO_4$ or likely in the outer coordination sphere of HPA-x with $3 \leq x \leq 6$. This follows from the similarity of the position of the maxima in curves $-\Delta_r H_{9j} = f(\alpha_j)$ (Figure 1), and $-\Delta_r H_{4j} = f(m_j)$ (Figures 2 and 3). However, the maxima in curves $-\Delta_r H_{4j} = f(m_j)$ are less sharp than in curve $-\Delta_r H_{9j} = f(\alpha_j)$. It seems that the enthalpy of reaction (10) in the outer coordination sphere of the heteropoly anion is probably less than in $HClO_4$ solution.

For 0.2 M HPA-1, HPA-2, and salts of HPA-3 solutions, there are no maxima in the $-\Delta_r H_{4j} = f(m_j)$ curves. This is associated with a low equilibrium concentration of VO_2^+ in these solutions. The ^{51}V-NMR spectra indicate that the VO_2^+ concentration is zero, < 0.01 M, and about 0.1 M in 0.2 M solution of HPA-1, HPA-2, and HPA-3, respectively.[26] The equilibrium concentration of VO_2^+ in solutions of HPA-x salts decreases with increasing pH.[34] Therefore, it is lower for solutions of HPA-3 salts than for those of HPA-3 itself. This explains the absence of maximum $-\Delta_r H_{4j} = f(m_j)$ on the reduction of HPA-3 salts solutions.

Values of $-\Delta_r H_4$ for solutions of VO_2HSO_4 and HPA-x in sulfate medium were found per 1 mole of HPA-x.[14] We recalculated them per 1 mole of HH, and found that they ranged from 679 to 879 kJ mol^{-1} HH. Rather high values of $-\Delta_r H_4$ for sulfate medium probably indicate, that complexes of SO_4^{2-} with VO^{2+}[20][21] are much stronger than with VO_2^+.[19]

The run of curves $-\Delta_r H_{4j} = f(m_j)$ for $H_{3+x}PV_xMo_{12-x}O_{40}$ solutions shows a definite sequence of reduction of different forms of vanadium(V) in these solutions. At lower m_j, the outer-sphere cation VO_2^+ is likely to be reduced first ($-\Delta_r H_{4j} = 431 \pm 14$ kJ mol^{-1} HH). For HPA-2, this quasi-free cation is reduced at $m_j \leq 0.5$. Note that the normal oxidation potential of VO_2^+ (aq.)/VO^{2+} (aq.) couple (1.00 V[22]) is higher than that of molybdovanadophosphates (from 0.68 to 0.715 V[29]). For HPA-x with $3 \leq x \leq 6$, it is reduced in the region of initial and maximal values of $-\Delta_r H_{4j}$. Vanadium(V) in the structure (inner sphere) of heteropoly anions $PV_yMo_{12-y}O_{40}^{(3+y)-}$ is reduced next. In this case, there is a region of curves $-\Delta_r H_{4j} = f(m_j)$ with a relatively small inclination (for HPA-2 and HPA-3) or relatively constant $-\Delta_r H_{4j} = 300 \pm 7$ kJ mol^{-1} HH (for HPA-4 and HPA-6). Figure 3 illustrates that this region has a longer length for HPA-6 than for HPA-4. We assume that the $H_{3+x+m}PV^{IV}{}_mV^{V}{}_{x-m}Mo_{12-x}O_{40}$ formed dissociates to eliminate vanadium(IV) as a quasi-free cation VO^{2+} [see Equation (8)]. Thus, the concentration of VO^{2+} in the outer sphere of heteropoly anions becomes higher than the initial concentration of VO_2^+ in the same sphere. (For HPA-2 solutions, this is also shown in ref.[35]) At the last stage, when m_j values are rather close to x, $-\Delta_r H_{4j}$ drops. In this stage, vanadium(V) in the structure of heteropoly anion is reduced without elimination of the cation VO^{2+}.

Oxidation of $H_{3+x+m}PV^{IV}{}_mV^{V}{}_{x-m}Mo_{12-x}O_{40}$ Solutions by Dioxygen

The calculated relationships $-\Delta_r H_{2j} = f(m_j)$ for oxidation of 0.2 M solutions of $H_{3+x+m}PV^{IV}{}_mV^{V}{}_{x-m}Mo_{12-x}O_{40}$ (H_mHPA-x) by dioxygen are shown in Figure 4. It follows from Equation (6) that changes in $-\Delta_r H_{2j}$ are always contrary to changes in $-\Delta_r H_{4j}$. For lower H_mHPA-x (x = 1, 2), the values of $-\Delta_r H_{2j}$ gradually decrease with decreasing m_j. For H_mHPA-x with $3 \leq x \leq 6$, they go through a minimum. For H_mHPA-x with x = 4 or 6, there is a region with relatively constant $-\Delta_r H_{2j}$ values (306 ± 7 kJ mol^{-1} O_2) at a rather high m_j (Figure 4). This region for oxidation of H_mHPA-x is similar to that for reduction of HPA-x (see Figure 3).

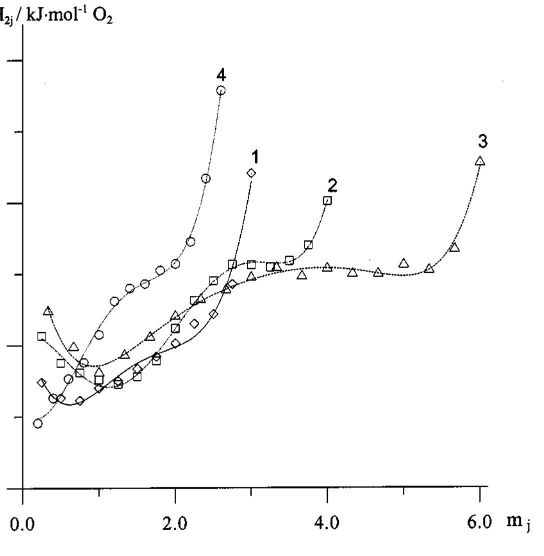

Figure 4. Differential enthalpies for reaction (2) vs. degree of reduction of HPA-x in 0.2 M aqueous solutions: 1: $H_{6+m}PV^{IV}{}_mV^{V}{}_{3-m}Mo_9O_{40}$; 2: $H_{7+m}PV^{IV}{}_mV^{V}{}_{4-m}Mo_8O_{40}$; 3: $H_{9+m}PV^{IV}{}_mV^{V}{}_{6-m}Mo_6O_{40}$; 4: $MgH_{5+m}PV^{IV}{}_mV^{V}{}_{4-m}Mo_8O_{40}$, $Na_2H_{5+m}PV^{IV}{}_mV^{V}{}_{4-m}Mo_8O_{40}$, and $K_2H_{5+m}PV^{IV}{}_mV^{V}{}_{4-m}Mo_8O_{40}$

We found earlier that the rates of reaction (2) decreased with decreasing m_j.[13] This means that changes in $-\Delta_rH_{2j}$ follow the changes in the rates of reaction (2).

The sequence of oxidation of different vanadium (IV) forms in $H_{3+x+m}PV^{IV}{}_mV^{V}{}_{x-m}Mo_{12-x}O_{40}$ solutions is evidently the reverse of the sequence of reduction of different vanadium (V) forms in $H_{3+x}PV_xMo_{12-x}O_{40}$ solutions. At the highest values of m_j, vanadium(IV) in the structure of anions $PV^{IV}{}_mV^{V}{}_{y-m}Mo_{12-y}O_{40}{}^{(3+x+m)-}$ is oxidized with high enthalpies $-\Delta_rH_{2j}$, which gradually decrease. Subsequently, at the middle values of m_j, the outer-sphere VO^{2+}, weakly bound with heteropoly anion $H_mHPA\text{-}x$, is oxidized to vanadium(V) which enters the structure of the heteropoly anion. (Outer-sphere complexes of the cation VO^{2+} with heteropoly anions are likely to be formed, for example, in dehydration of hydrated VO^{2+} salts of $H_4SiW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ at 423 to 523 K.[36]) Such regions are observed for HPA-x with $2 \le x \le 6$. At the lowest m_j, the outer sphere VO^{2+} is oxidized to $VO_2{}^+$ with the lowest $-\Delta_rH_{2j}$ values (from 120 to 180 kJ mol^{-1} O_2) remaining in the outer sphere. Cations $VO_2{}^+$ and VO^{2+} in the outer sphere of the heteropoly anion can probably interact reversibly with each other to yield mixed valence cations.

Thus, the thermochemical study of the $H_{3+x}PV_xMo_{12-x}O_{40}$ reduction and the $H_{3+x+m}PV^{IV}{}_m$-$V^{V}{}_{x-m}Mo_{12-x}O_{40}$ oxidation in aqueous solutions proves that the composition of heteropoly anions changes reversibly in the course of reactions (1) and (2).[11] In these conversions, the cations $VO_2{}^+$ and VO^{2+} participate and can also interact in the outer coordination sphere of the heteropoly anion.

Experimental Section

We used HPA-x solutions containing no foreign anions which could act as complexing agents. Reaction (4) was carried out at 343 ± 0.1 K for 5 to 15 min. Under these conditions, the effect of uncontrolled factors on measuring data was minimal.

For preparing 0.2 M aqueous solutions of $H_{3+x}PV_xMo_{12-x}O_{40}$ (HPA-x, $1 \le x \le 6$), the reaction of H_3PO_4 and MoO_3 with an aqueous solution of $H_6V_{10}O_{28}$ was used.[26] The initial pH value of the HPA-x solutions (hereafter designated as pH_0) ranged from 0.35 to 0.4. For preparing 0.2 M solutions of HPA-3 salts of $M^{I}{}_2H_4PMo_9V_3O_{40}$ composition, metal carbonates were dissolved in the 0.2 M solution of HPA-3. Values of the pH of prepared solutions (HPA-x and their salts) were measured using a digital ionometer I-130.

For preparing 0.1 M solutions of VO_2ClO_4 in $HClO_4$, V_2O_5 was dissolved in cold 5% H_2O_2;[37] the solutions of the peroxyvanadium compounds produced were decomposed to yield O_2 and $H_6V_{10}O_{28}$,[37] which was transformed to VO_2ClO_4 using the calculated amount of $HClO_4$. An analogous 0.2 M solution of VO_2ClO_4 in 1 M $HClO_4$ could not be prepared either by our method or by the direct dissolution of V_2O_5 in $HClO_4$.[38] Hydrazine hydrate (of analytical grade purity) was used as a ca. 10 M aqueous solution, whose precise concentration was determined by iodometry.[39]

Our experiments were carried out in a thermostated Thiane-Calvet glass reactor-calorimeter[40] (150 mL in volume), equipped with a stirrer. The reactor was adapted to studies of liquid-phase reactions. The high sensitivity of the calorimeter was provided by two sensors (thermocouple batteries) connected towards each other. The sensors measured the temperature difference between the inner reactor part and the outer thermostated water and the sensor signals were then magnified and registered by an integrator. The heat released in the reactor was proportional to the temperature difference and the duration of heat liberation, recorded by the integrator. The gas space of the reactor was connected to a thermostated burette for measuring the volume of released dinitrogen. The proportionality coefficient K between the released heat q_{4i} and a number of heat pulses k_i on the integrator was found by a current calibration of the reactor-calorimeter. One pulse of the integrator corresponded to 0.0335 J. The average error of the q_{4i} measurements was within ± 2%. The volume of dinitrogen released, V_{gi}, was recalculated to the number of moles n_{gi}.

Each solution under study (HPA-x or VO_2ClO_4) was tested in 3−5 runs in dinitrogen, q_{4i} and V_{gi} being measured. During a run, 7−12 small portions of HH solution (thoroughly agitated) were injected through a rubber membrane into the reactor, containing 100 mL of the solution being under study. This permitted a stepwise increase of m_i, allowing calculation of differential enthalpies $-\Delta_rH_{4i}$ per mole of HH, which depend on the instantaneous m_i. We used fresh solutions of HPA-x as well as those reoxidized by dioxygen or H_2O_2. Since the heat of dilution of ca. 10 M HH solution is below 8.6 kJ mol^{-1},[41] it does not exceed the errors of our measurements and we therefore did not take it into account.

All heat effects were observed only in the course of dinitrogen liberation. The number of moles of released nitrogen, n_{gi}, was equal to that of introduced HH with an accuracy of ± 1%. This proves that vanadium(V) in the HPA-x solution was reduced stoichiometrically by Equation (4a), and any side conversions of HH did not occur.

$$4\,[V^{V}]_{HPA\text{-}x} + N_2H_4{\cdot}H_2O \rightarrow 4\,[V^{IV}]_{H_mHPA\text{-}x} + 4\,H^+ + H_2O + N_2\uparrow \qquad (4a)$$

When the reactor contained $n_L = C_LV_L$ moles of HPA-x, the degree of reduction of HPA-x increased to $m_i = m_{i-1} + 4\,n_{gi}/n_L$ after the ith injection of HH. The measured differential heats, $q_{4i} = K{\cdot}k_i$ were related to the average degree of HPA-x reduction $m_i = 0.5\,(m_{i-1} + m_i)$. The enthalpy of reaction (4a) was calculated in all cases for 1 mole of dinitrogen (HH, respectively): $\Delta_rH_{4i} = -q_{4i}/n_{gi}$.

The sum of reactions (4) and (2) corresponds to reaction (5). At 343 K, the enthalpy of this reaction, Δ_rH_5, was calculated from the standard formation enthalpies of H_2O and $N_2H_4{\cdot}H_2O$,[22] and is approximately equal to 606 kJ·mol^{-1} (Equation 11).

$$\Delta_rH_2 = -606 - \Delta_rH_4 \qquad (11)$$

The m_i and corresponding Δ_rH_{4i} and Δ_rH_{2i} values were calculated using a special computer program. To interpolate $\Delta_rH_{4i} \rightarrow \Delta_rH_{4j}$ and $\Delta_rH_{2i} \rightarrow \Delta_rH_{2j}$, we used the standard programs for uniformly distributed m_j, followed by averaging for several runs. The interpolation errors were below ± 2.5%. The total error for Δ_rH_{4j} and Δ_rH_{2j} did not exceed ± 4.5%.

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