Oxygen Exchange between Oxo-anions and Water in Basic Media: Molybdate(2−) and Tungstate(2−)

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The ^{18}O-exchange reaction between $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ respectively and water has been investigated in alkaline solutions at constant total concentration of ionic equivalents $J = 1.0$ mol dm^{-3} (Na[ClO$_4$]). Over the range $3 \times 10^{-3} \leqslant [OH^-] \leqslant 1.5 \times 10^{-1}$ mol dm^{-3} at 5 °C ($[MoO_4]^{2-}$) and $2 \times 10^{-3} \leqslant [OH^-] \leqslant 7.5 \times 10^{-3}$ mol dm^{-3} at 1 °C ($[WO_4]^{2-}$) the exchange occurs by spontaneous and hydroxide-ion catalyzed paths (X = Mo or W) according to the rate equation (i). The rate constants extrapolated at 25 °C are $k_0 = 0.33$ s^{-1} and $k_1 = 2.22$ dm^3

$$R/[XO_4{}^{2-}]_T = k_0 + k_1[OH^-] \qquad \text{(i)}$$

mol^{-1} s^{-1} for $[MoO_4]^{2-}$ and $k_0 = 0.44$ s^{-1} and $k_1 = 273$ dm^3 mol^{-1} s^{-1} for $[WO_4]^{2-}$. The following activation parameters were obtained: $\Delta H_0{}^\ddagger = 62.8 \pm 2.5$ kJ mol^{-1}, $\Delta S_0{}^\ddagger = -43.5 \pm 9.0$ J K^{-1} mol^{-1}, $\Delta H_1{}^\ddagger = 70.3 \pm 5.0$ kJ mol^{-1}, and $\Delta S_1{}^\ddagger = -2.5 \pm 13.0$ J K^{-1} mol^{-1} ($[MoO_4]^{2-}$); and $\Delta H_0{}^\ddagger = 29.25 \pm 3.22$ kJ mol^{-1}, $\Delta S_0{}^\ddagger = -153.55 \pm 11.30$ J K^{-1} mol^{-1}, $\Delta H_1{}^\ddagger = 71.1 \pm 8.0$ kJ mol^{-1}, $\Delta S_1{}^\ddagger = 40.2 \pm 28.9$ J K^{-1} mol^{-1} ($[WO_4]^{2-}$). The values for the kinetic solvent deuterium-isotope effects $k_0{}^H/k_0{}^D = 3.6$ and $k_1{}^H/k_1{}^D = 2.3$ (5 °C, $[MoO_4]^{2-}$) and $k_0{}^H/k_0{}^D = 3.0$ and $k_1{}^H/k_1{}^D = 1.7$ (1 °C, $[WO_4]^{2-}$), indicate proton transfer in the rate-determining step. The mechanisms of the spontaneous paths are described as solvent-assisted oxygen dissociations with association between H_2O and $[XO_4]^{2-}$ playing an important role, whereas the $[OH]^-$-dependent paths are tentatively viewed as associative reactions between $[OH]^-$ and $[XO_4]^{2-}$.

THE simple oxygen-exchange reaction (1) between oxo-anions and solvent water can obviously be compared

$$n\,H_2{}^*O + [XO_n]^{z-} \rightarrow n\,H_2O + [X^*O_n]^{z-} \qquad (1)$$

with the exchange of ligand and solvent water occurring on a metal ion in aqueous solutions [equation (2)].

$$6\,H_2{}^*O + [M(OH_2)_6]^{m+} \rightarrow 6\,H_2O + [M(^*OH_2)_6]^{m+} \qquad (2)$$

Water exchange is one of the most important substitution reaction processes in inorganic chemistry [1] and has been studied for many cations in detail, the rates varying over 18—20 orders of magnitude. Much less is known about the exchange processes for oxo-anions [equation (1)]. For oxo-anions of transition metals, so far only the isotopic oxygen exchange of vanadate,[2] chromate,[3] permanganate,[4] manganate,[4] and perrhenate [5] with water has been investigated quantitatively. Hall and Alexander [6] reported complete exchange of oxygen between water and molybdate and tungstate respectively within 1 h at 95—100 °C. Geier and Brubaker [7] published some results on the oxygen exchange of tungstate. The experiments were carried out at 25 °C and pH 11—12 and showed complete exchange within the time needed for mixing and separation (*ca.* 45—50 s). So far no quantitative results on the $[MoO_4]^{2-}$–H_2O exchange have been reported.

We have made a detailed kinetic investigation of reaction (1) using ^{18}O-labelling techniques. For reaction intervals >50 s found in the $[MoO_4]^{2-}$–H_2O system a conventional procedure was applied. Some of the faster exchange reactions of tungstate and water were studied by combining ^{18}O labelling with rapid chemical quenching. All the reactions were carried out in a pH range where hydrolysis and polymerization of both $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ are negligible.[8]

EXPERIMENTAL

Materials.—For the preparation of the reactant solutions, $Na_2[MoO_4]\cdot 2H_2O$ and $Na_2[WO_4]\cdot 2H_2O$ were used respectively; for the molybdate and tungstate solutions in D_2O, the sodium compounds were dehydrated to prevent a dilution of the deuterium content. Sodium perchlorate was prepared from sodium carbonate and perchloric acid. All the substances were reagent grade (E. Merck) and were used without further purification. High-purity ^{18}O-labelled $H_2{}^*O$ (5% ^{18}O, 0.5% ^{17}O, 0.15% D), $D_2{}^*O$ (99.97% D, 6.55% ^{18}O), and solvent D_2O (99.85% D, 1.8% ^{18}O) were obtained from the isotope-separation facilities of the E. I. R. Water having its normal isotopic composition was double distilled using an all-quartz apparatus.

Procedure.—(*a*) *Conventional method.* All the exchange experiments in the system $[MoO_4]^{2-}$–H_2O and in $[WO_4]^{2-}$–H_2O at low temperatures (1 and 5 °C) were carried out by a conventional technique. The reactant solutions were kept at constant total concentration of ionic equivalents,[9] *J*, rather than at constant ionic strength. The exchange reactions were initiated by mixing unlabelled solutions of known hydroxide concentration with ^{18}O-labelled molybdate or tungstate solutions, also containing known hydroxide concentrations, in test tubes (10 cm^3). The metallate solutions were obtained by equilibration with labelled $H_2{}^*O$ (5% ^{18}O) for at least 0.5 h. The ionic equivalents were kept constant using Na[ClO$_4$]. After definite time intervals the reactions were stopped by addition of 0.2 mol dm^{-3} Ba[ClO$_4$]$_2$ in ethanol.

(*b*) *Rapid quenching.* The faster exchange reactions of tungstate at higher temperatures were carried out using the Multi-Mixing-System.[10,11] With this equipment, reaction-

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[1] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 657.

[2] R. K. Murmann, *Inorg. Chem.*, 1977, **16**, 46.

[3] M. R. Baloga and J. E. Earley, *J. Phys. Chem.*, 1963, **67**, 964; R. H. Holyer and H. W. Baldwin, *Canad. J. Chem.*, 1967, **45**, 413.

[4] H. O. McDonald, *Diss. Abs.*, 1960, **21**, 454; K. H. Heckner and R. Landsberg, *J. Inorg. Nuclear Chem.*, 1967, **29**, 413.

[5] R. K. Murmann, *J. Phys. Chem.*, 1967, **71**, 974.

[6] N. F. Hall and O. R. Alexander, *J. Amer. Chem. Soc.*, 1940, **62**, 3455.

[7] G. Geier and C. H. Brubaker, *Inorg. Chem.*, 1966, **5**, 321.

[8] C. F. Baes, jun., and R. E. Mesmer, 'The Hydrolysis of Cations,' Wiley, New York, 1976.

[9] L. Johannson, *Acta Chem. Scand.*, 1975, **A29**, 365.

[10] H. v. Felten, H. Gamsjäger, and P. Baertschi, *J.C.S. Dalton*, 1976, 1683; H. v. Felten, Ph.D. Thesis, University of Berne, 1976.

[11] H. v. Felten and H. Gamsjäger, *Proc. Internat. Conf. Coordination Chem.*, 1976, **17**, 40.

time intervals can be continuously varied from 2×10^{-2} to 11 s. Tungstate solutions were mixed with an equal volume of ^{18}O-labelled water, both solutions having been adjusted to the appropriate hydroxide concentration and ionic equivalents with Na[OH] and $Na[ClO_4]$ respectively. After preselected time intervals the exchange reactions were quenched by rapid addition of 0.2 mol dm^{-3} $Ba[ClO_4]_2$ in ethanol.

The $Ba[Mo^*O_4]$ ($Ba[W^*O_4]$) precipitate was centrifuged, washed carefully with water, ethanol, and acetone, and dried at 80 °C. Figure 1 shows the apparatus used for pyrolysis and collection of the CO samples. About 10 mg of $Ba[Mo^*O_4]$ ($Ba[W^*O_4]$) were carefully mixed with an equal amount of graphite and placed in a graphite crucible fixed on a molybdenum rod. The quartz tube containing the crucible, a cooling trap, and a Toepler pump were connected to a vacuum line. Inductive heating was effected by a helical coil connected to a 1.5-kW radio-frequency generator. First, the water was removed by degassing at 800 °C, then the system was again evacuated and $Ba[Mo^*O_4]$ or $Ba[W^*O_4]$ was decomposed at 1 400 °C to give mainly CO. The small amount of CO_2 was frozen in the trap with liquid nitrogen. The CO gas was sampled using the Toepler pump and isotopically analyzed with a cycloidal CEC 21-620 A mass spectrometer. The mass spectra of the isotopic oxygen molecules were scanned three times in order to reduce the errors in peak-height measurements to less than 0.5%. Exchange rates were measured at 4—6 different time intervals. In order to show that precipitation of the barium salts completely stops the exchange process a solution of molybdate equilibrated with $H_2{}^{18}O$ was precipitated as $Ba[Mo^*O_4]$ and analyzed as above. The mol fraction of ^{18}O in the $Ba[Mo^*O_4]$ agreed within experimental error with the calculated value. A similar rigorous check could not be applied to the tungstate experiments, since a fraction of induced exchange occurred, and varied with $[OH^-]$.

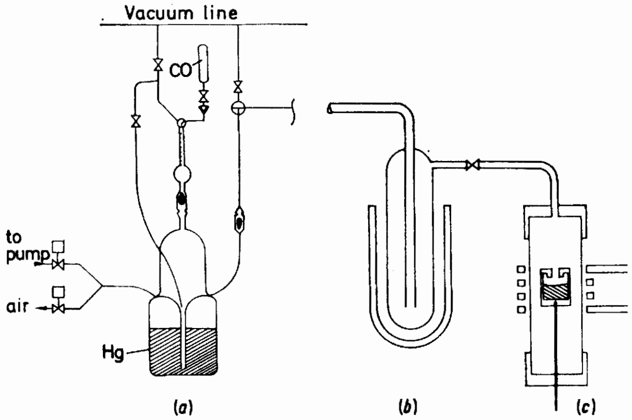

FIGURE 1 Apparatus for decomposition: (*a*) Toepler pump; (*b*) cooling trap; and (*c*) quartz tube with graphite crucible and induction heating. Diagrams (*b*) and (*c*) are expanded

Calculation of Results.—Actual hydroxide-, molybdate-, and tungstate-ion concentrations were calculated from the analytical composition of the reactant solutions. The mol fractions, *x*, of ^{18}O in the gaseous CO samples submitted to mass-spectrometric analysis were calculated from peak heights at *m/e* 28—31. The rate of reaction (1) leading to isotopic exchange was calculated from the simplified McKay[12] expression (3), where *R* is the rate of oxygen transfer between H_2O and $[MoO_4]^{2-}$ or $[WO_4]^{2-}$ respectively,

$$\frac{R}{[XO_4{}^{2-}]_T} = k_{\text{obs.}} = \frac{4}{t}\ln\frac{x_\infty - x_0}{x_\infty - x_t} \qquad (3)$$

in mol dm^{-3} s^{-1}, X = Mo or W, *t* is the time in s, and x_0 x_t, and x_∞ are the mol fractions of ^{18}O in molybdate and tungstate respectively at time $t = 0$, t = time of quenching, and $t = \infty$ (at exchange equilibrium). Values of x_∞ were determined separately by analyzing isotopically equilibrated solutions. Regression analysis of all the data was performed on an HP 2000A time-sharing computer. Errors in rate constants and activation parameters are standard deviations.

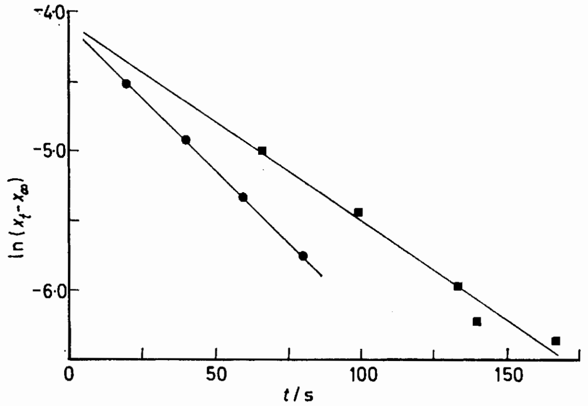

FIGURE 2 McKay plots for the oxygen exchange in the system $[MoO_4]^{2-}$–H_2O at 5 °C and $J = 1$ mol dm^{-3} ($Na[ClO_4]$). $[OH^-] = 9.99 \times 10^{-3}$ (■) or 0.1 mol dm^{-3} (●)

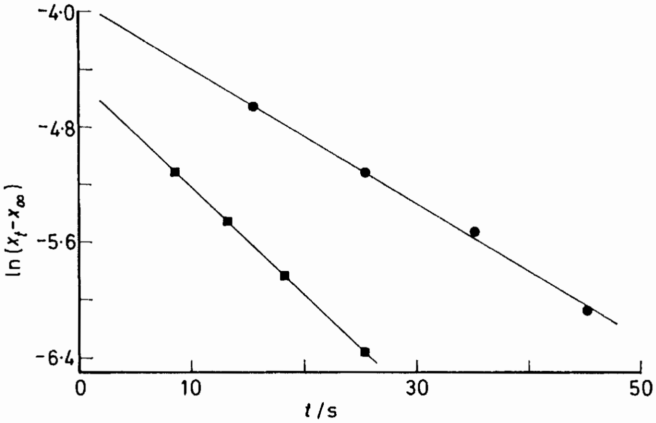

FIGURE 3 McKay plots for the oxygen exchange in the system $[WO_4]^{2-}$–H_2O at 1 °C and $J = 1$ mol dm^{-3} ($Na[ClO_4]$). $[OH^-] = 1.99 \times 10^{-3}$ (●) or 7.5×10^{-3} mol dm^{-3} (■)

RESULTS

Plots of ln $(x_t - x_\infty)$ against time were linear up to 90% completion of exchange in the case of the conventional method. The scatter inherent in the Multi-Mixing technique resulted in linear plots of ln $(x_t - x_\infty)$ against *t* which were reliable only to 70% completion; therefore in this case only data measured at $t < 2t_{\frac{1}{2}}$ have been included in the calculation of rates. Figures 2 and 3 show typical McKay plots. In the $[MoO_4]^{2-}$–H_2O exchange the intercepts $\ln(x_t - x_\infty)$ are independent of the prevailing hydroxide

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[12] H. A. C. McKay, *Nature*, 1938, **142**, 997.

concentration. For tungstate remarkably different intercepts were observed, however, and the portion of exchange induced increased from 30 to 70% with increasing hydroxide concentration. Since the gradients and intercepts of the plots were fully reproducible this effect was interpreted as a zero-time exchange or an exchange induced by the precipitation step and consequently $k_{obs.}$ was calculated from the gradients of the straight lines as with molybdate. A similar situation was also observed in the Tl^I–Tl^{III} exchange.[13] When $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ are acidified both ions polymerize and give complicated series of isopolyanions depending on the reaction conditions.[8] Because we were primarily interested in the oxygen exchange of simple $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ and solvent water we restricted our experiments to the alkaline region.

TABLE 1

Relative rates of exchange, $k_{obs.}$, in the system $[MoO_4]^{2-}$–H_2O at 5 °C and $J = 1$ mol dm^{-3} ($Na[ClO_4]$) where $J = \frac{1}{2}(\sum_i C_i|z_i|)$ (ref. 9)

Run	$10^2[MoO_4^{2-}]_T$	$10^3[OH^-]$	$10^2 k_{obs.}$
	mol dm^{-3}	mol dm^{-3}	s^{-1}
1	6.29	3.23	5.53
2	3.14	5.0	5.67
3	6.29	5.0	5.55
4	12.6	5.0	5.77
5	6.29	9.99	5.71
6	6.29	40.0	6.69
7	6.29	75.7	7.32
8	6.29	100.0	8.23
9	6.29	150.2	9.66

The pertinent data for the oxygen exchange between molybdate and water at 5 °C are collected in Table 1. The quantity $R/[MoO_4^{2-}]_T = k_{obs.}$ is independent of $[MoO_4^{2-}]$ and gives a linear dependence on $[OH^-]$, with an intercept significantly different from zero indicating a spontaneous path in the exchange reaction. Thus for the oxygen exchange between $[MoO_4]^{2-}$ and water at 5 °C and $J = 1$ mol dm^{-3} ($Na[ClO_4]$) the rate equation (4) is valid where

$$R/[MoO_4^{2-}]_T = k_0 + k_1[OH^-] \qquad (4)$$

TABLE 2

Relative rates of exchange, $k_{obs.}$, in the system $[MoO_4]^{2-}$–H_2O at different temperatures, $J = 1$ mol dm^{-3} ($Na[ClO_4]$), and $[MoO_4^{2-}] = 0.062\,9$ mol dm^{-3}

Run	$10^2[OH^-]$	T	$k_{obs.}$
	mol dm^{-3}	K	s^{-1}
10	0.5	273.85	0.035 9
11	0.5	283.15	0.095 3
12	0.5	288.15	0.161
13	0.5	293.15	0.227
14	15.0	273.85	0.060 1
15	15.0	276.15	0.076 4
16	15.0	280.70	0.12
17	15.0	283.15	0.163

$k_0 = (5.43 \pm 0.07) \times 10^{-2}$ s^{-1} and $k_1 = 0.278 \pm 0.009$ dm^3 mol^{-1} s^{-1}. The results of exchange experiments at different temperatures are summarized in Table 2. The experiments at $[OH^-] = 5 \times 10^{-3}$ mol dm^{-3} gave preliminary k_0 values because at this hydroxide concentration the contribution of the k_1 term is almost negligible. The calculation of the final k_0 and k_1 values was based on an iterative procedure. Linear Eyring plots of the rate constants k_0 and k_1 were obtained and the activation parameters computed by regression analysis are $\Delta H_0^‡ = 62.8 \pm 2.5$ kJ mol^{-1}, $\Delta S_0^‡ = -43.5 \pm 9.0$ J K^{-1} mol^{-1}, $\Delta H_1^‡ = 70.3 \pm 5.0$ kJ mol^{-1}, and $\Delta S_1^‡ = -2.5 \pm 13.0$ J K^{-1} mol^{-1}.

TABLE 3

Relative rates of exchange, $k_{obs.}$, in the system $[WO_4]^{2-}$–H_2O at $J = 1$ mol dm^{-3} ($Na[ClO_4]$)

Run	T	$10^2[WO_4^{2-}]$	$10^3[OH^-]$	$k_{obs.}$
	K	mol dm^{-3}	mol dm^{-3}	s^{-1}
18	274.15	3.00	1.99	0.187
19		6.00	1.99	0.187
20		12.00	1.99	0.196
21		6.00	3.01	0.195
22		6.00	4.55	0.229
23		6.00	5.99	0.247
24		6.00	7.5	0.295
25	278.15	6.00	1.99	0.233
26		6.00	3.1	0.265
27		6.00	4.55	0.32
28		15.00	7.5	0.397
29	283.15	15.00	1.99	0.324
30		15.00	3.1	0.369
31		15.00	4.55	0.456
32		15.00	7.5	0.566
33	288.15	15.00	1.99	0.463
34		15.00	3.1	0.609
35		15.00	4.55	0.674
36		15.00	7.5	1.019

Table 3 contains the experimental data for the oxygen exchange between $[WO_4]^{2-}$ and water. Again plots of $R/[WO_4^{2-}]_T$ against $[OH^-]$ indicate a linear dependence with a non-zero intercept. R showed a first-order dependence on $[WO_4^{2-}]$. The experimental data are consistent with rate equation (5) which is completely analogous to (4).

$$R/[WO_4^{2-}]_T = k_0 + k_1[OH^-] \qquad (5)$$

At $J = 1$ mol dm^{-3} ($Na[ClO_4]$) and 1 °C, $k_0 = 0.142 \pm 0.010$ s^{-1} and $k_1 = 19.2 \pm 2.0$ dm^3 mol^{-1} s^{-1}. Eyring plots of the k_0 and k_1 values were linear and the activation parameters were $\Delta H_0^‡ = 29.25 \pm 3.22$ kJ mol^{-1}, $\Delta S_0^‡ = -153.55 \pm 11.30$ J K^{-1} mol^{-1}, $\Delta H_1^‡ = 71.1 \pm 8.0$ kJ mol^{-1}, and $\Delta S_1^‡ = 40.2 \pm 28.9$ J K^{-1} mol^{-1}.

TABLE 4

Relative rates of exchange in the systems $[MoO_4]^{2-}$–D_2O and $[WO_4]^{2-}$–D_2O at $J = 1$ mol dm^{-3} ($Na[ClO_4]$)

Run	$10^2[OD^-]$	$10^2[MoO_4^{2-}]$	$10^2[WO_4^{2-}]$	T	$10^2 k_{obs.}$
	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	K	s^{-1}
37	0.2	6.29		278.15	1.52
38	10.0	6.29		278.15	2.71
39	0.266		6.00	274.15	7.53
40	0.601		6.00	274.15	12.1
41	1.00		6.00	274.15	16.1

A four-fold variation of both $[MoO_4^{2-}]$ and $[WO_4^{2-}]$ at low constant $[OH^-]$ caused no significant change in $k_{obs.}$ (runs 2—4 and 18—20) indicating the absence of base impurities in the starting materials. In another series of experiments (Table 4) water was replaced by D_2O as solvent. The general form of the rate equation in D_2O was the same as in water [equation (4) or (5)]. Runs 37 and 38 allow the determination of the rate constants in D_2O for molybdate at 5 °C: $k_0^D = 0.015\,2$ s^{-1}, $k_1^D = 0.119$ dm^3 mol^{-1} s^{-1}. The rate constants of the $[WO_4]^{2-}$–D_2O exchange can be calculated from experiments 39—41. At 1 °C they are $k_0^D = 0.047$ s^{-1} and $k_1^D = 11.5$ dm^3 mol^{-1} s^{-1}. The

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[13] R. J. Prestwood and A. C. Wahl, *J. Amer. Chem. Soc.*, 1949, **71**, 3137.

values for the kinetic solvent-isotope effects are $k_0{}^{H}/k_0{}^{D} = 3.6$ and $k_1{}^{H}/k_1{}^{D} = 2.3$ for the oxygen exchange between $[MoO_4]^{2-}$ and water at 5 °C, and $k_0{}^{H}/k_0{}^{D} = 3.0$ and $k_1{}^{H}/k_1{}^{D} = 1.7$ for the oxygen exchange between $[WO_4]^{2-}$ and water at 1 °C.

DISCUSSION

Both systems investigated show similar rate equations (4) and (5) for the oxygen exchange in basic media. In neither system was the reaction order with respect to the concentration of water studied. It is therefore difficult to assess unambiguously whether the mechanisms follow an I_a or I_d type of activation. For the spontaneous exchange paths of tungstate, molybdate, and vanadate [2] a plot of $\Delta H_0{}^{\ddagger}$ against $\Delta S_0{}^{\ddagger}$ is linear as shown in Figure 4, with an isokinetic temperature [14] of 277 ± 13 K.* This indicates a common rate-determining step in excellent agreement with the prediction of Murmann.[2] The ionic radii of W^{VI}, Mo^{VI}, and V^{V} are very similar; according to one source [15,16] they decrease in the order W^{VI} (0.65), Mo^{VI} (0.62), V^{V} (0.59 Å) and so do the rates in the $\Delta H_0{}^{\ddagger}$-controlled temperature range. However, if the effective ionic radii (W^{VI}, 0.41; Mo^{VI}, 0.42; V^{V}, 0.355 Å) according to the comprehensive compilation of Shannon and Prewitt [17] are used this correlation is no longer valid. The mechanism can probably be described as solvent-assisted oxygen dissociation [5] (X = W or Mo) where association between water and $[XO_4]^{2-}$ plays an important role. The rapid complexation of molybdate with the substitution-inert pentaammineaquacobalt(III) given by (6) was studied by

$$[Co(NH_3)_5(OH)]^{2+} + [HMoO_4]^{-} \longrightarrow [Co(NH_3)_5(MoO_4)]^{+} + H_2O \quad (6)$$

Taylor [18] at a different pH range (7.1—8.0). For comparison with the data reported here, we considered the possibility that the k_a path in ref. 18 corresponds not to reaction (6) but rather to reaction (7) where the water

$$[Co(NH_3)_5(OH_2)]^{3+} + [MoO_4]^{2-} \longrightarrow [Co(NH_3)_5(MoO_4)]^{+} + H_2O \quad (7)$$

reacting with molybdate is already co-ordinated to a metal ion. However, k_a exceeds $k_0/[H_2O]$ by a factor of $>10^4$ and no evidence was found supporting a large ion-pair formation constant, in fact a value of $K_0 < 1$ dm^3 mol^{-1} was estimated.[18] This suggests that different mechanisms are operating for complex formation and oxygen exchange of $[MoO_4]^{2-}$ due to the different pH range used in the latter study. At lower pH values, however, there may well be other paths, *e.g.* involving $[HMoO_4]^{-}$, which contribute to the oxygen exchange of molybdate and water.

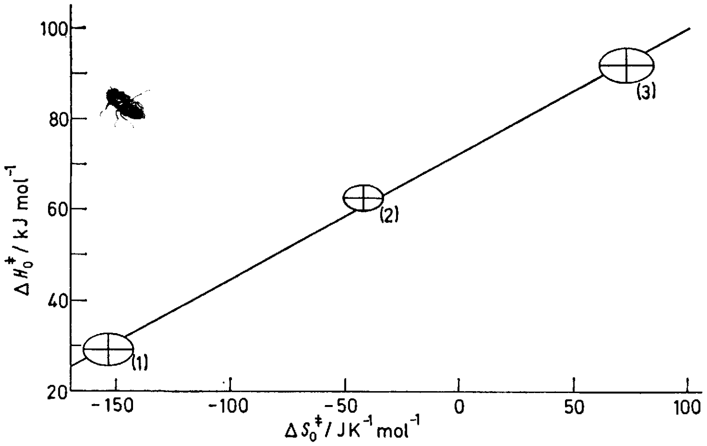
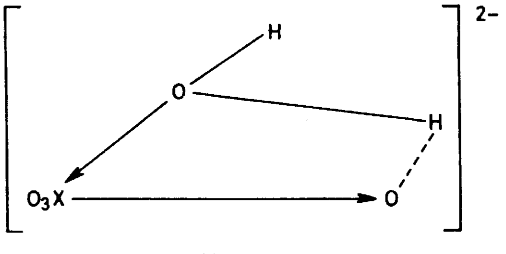


FIGURE 4 Isokinetic plot for the anions $[WO_4]^{2-}$ (1), $[MoO_4]^{2-}$ (2), and $[VO_4]^{3-}$ (3)



Normal solvent-isotope effects found for the spontaneous exchange paths indicate proton transfer occurring in the rate-determining step, the numerical values of $k_0{}^{H}/k_0{}^{D}$ being in line with solvent-isotope effects of similar reactions.[19] Molybdate as well as $[WO_4]^{2-}$ showed an $[OH]^{-}$-catalyzed exchange path whereas $[VO_4]^{3-}$ did not. This may be due to the higher charge on $[VO_4]^{3-}$ which makes it increasingly difficult for $[OH]^{-}$ to attack the

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* It should be emphasized that the value of $\Delta S^{\ddagger}$ varies by $\pm R$ ln (number of oxygen atoms in the oxo-anion) depending on the definition of $k_{obs.}$ according to equation (3). Therefore Murmann's results [2] had to be recalculated for comparison with our data.

[14] R. G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes,' Allyn and Bacon, Boston, 1974, p. 100.

[15] G. A. Tsigdinos, 'Heteropoly Compounds of Molybdenum and Tungsten,' Climax Molybdenum Company, Bulletin Cdb-12 (revised), November 1969.

[16] L. Pauling, 'The Nature of Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 514.

[17] R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, 1969, **B25**, 925.

[18] R. S. Taylor, *Inorg. Chem.*, 1977, **16**, 116.

[19] H. Gamsjäger, A. Grütter, and P. Baertschi, *Helv. Chim. Acta*, 1972, **55**, 871.

anion. Again the normal solvent-isotope effects observed point to proton transfer occurring in the rate-determining step. The values of k_1^H/k_1^D are remarkably smaller than k_0^H/k_0^D. This seems to be a common feature of oxygen-exchange reactions since the same result was obtained with bromate.[19] Probably this simply reflects that one and two O–H bonds are involved in the $[OH]^-$-catalyzed and the spontaneous exchange paths respectively. Since Mo^{VI} and W^{VI} expand their co-ordination numbers easily the $[OH]^-$-dependent exchange paths are tentatively viewed as associative reactions between $[OH]^-$ and the respective oxo-anion.

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