153. The Solution Structure and Reactivity of Decavanadate

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The oxygen-exchange reaction of $V_{10}O_{28}^{6-}$ with bulk water has been followed by time-dependent ^{17}O-NMR spectroscopy (buffered solutions, pH ~ 5.5, $[V_{10}]_{total} \sim 0.17m$, $T = 298$ K). It is shown that all seven structurally different sites of O-atoms are kinetically similar but, in contrast to earlier studies, not identical (6 h $\leqslant$ '$t_{1/2}$' $\leqslant$ 11 h). The kinetic similarity of the various structural sites implies that some (but not full) O scrambling is involved. Two possible mechanisms with a 'half-bonded' and an 'open' intermediate are discussed in detail to interpret the experimental results. A computer simulation of the exchange reaction based on these models is presented. It is shown that the 'half-bonded-intermediate' mechanism is consistent with the experimental data and the following parameters are calculated: formation of the intermediate: $k_1 = 5.8 \cdot 10^{-3}$ s^{-1}, $k_{-1} = 6.7 \cdot 10^{-2}$ s^{-1}, [intermediate]$_\infty \approx 8\%$; all activated O-atoms exchange within the lifetime of the intermediate ($\tau \sim 15$ s), and the calculated exchange rate of the intermediate ($k_2 \geqslant 0.60$ s^{-1}) is consistent with earlier assumptions ($k_2 \approx 0.5$ s^{-1}). It is shown that a simulation based on the 'open-intermediate' mechanism results in kinetic parameters which are not consistent with the kinetics of the formation of cyclic metavanadates ($(VO_3^-)_n$, $n = 4,5$) from decavanadate, since the required formation rate is by a factor $\sim 10^2$ too fast, and the equilibrium concentration of metavanadates is by a factor of ~ 2 too large (under the conditions of the O-exchange experiments of decavanadate ($T = 298$ K, $[V_{10}]_{total} \approx 0.17m$, pH ~ 5.55) the total amount of metavanadates present is ~ 8%, with $[(VO_3^-)_4]/[(VO_3^-)_5] \sim 4{:}1$; a qualitative analysis of the kinetics of the formation of metavanadates (v_0 kinetics; the exact mechanism of the back-reaction (at least second-order) is not known with certainty) leads to $k_1 \geqslant 4 \cdot 10^{-5}$ s^{-1}). O exchange of decavanadate *via* equilibrated metavanadates would lead to full scrambling of the O sites and is not consistent with the observed differences in the exchange rates. From the qualitative kinetic parameters of the metavanadate formation kinetics, it can be concluded that any contribution of an 'open' or a 'metavanadate' mechanism is of the order of 1–2% at most.

Introduction. – Vanadium and particularly its V(V) oxidation state are recently attracting increasing interest because of their biological relevance. It is now known that vanadates interact with a large class of phosphatases and phosphotransferases, and that they are partly able to mimic orthophosphate [1]. The system of aqueous vanadates is very complex, since ortho- as well as metavanadates form a large number of mono- and polymeric hydrolysis products, and the composition of aqueous vanadate solutions is pH- as well as $[V(V)]_{total}$-dependent [2–10].

The isopolyanion $V_{10}O_{28}^{6-}$ is the largest condensation product in the system, and its solid-state structure is well known [11–14]. The solution structure of $V_{10}O_{28}^{6-}$ has been studied in some detail by ^{17}O- and ^{51}V-NMR spectroscopy [14–19], and it was confirmed that the solution structure is qualitatively identical to the solid-state structure *(Fig. 1, a)*.

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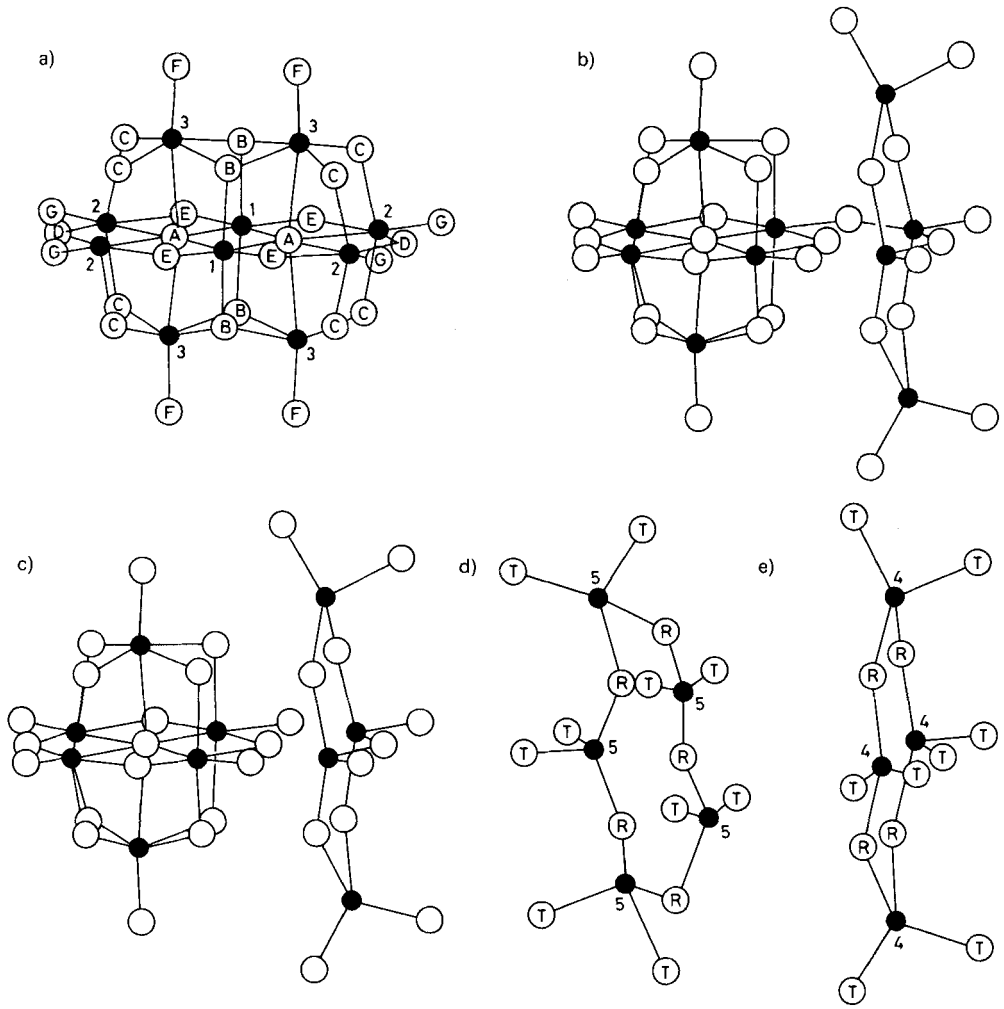

Fig. 1. *Structures and labelling of decavanadate, activated intermediates, and metavanadates.* *a)* Decavanadate; *b)* 'half-bonded' intermediate; *c)* 'open' intermediate; *d)* $(VO_3^-)_4$; *e)* $(VO_3^-)_5$.

There are seven types of structurally different O-atoms (A–G) and three types of structurally different V-atoms (1–3). Their NMR resonances are fully assigned [18].

Aqueous solutions of $V_{10}O_{28}^{6-}$ contain, depending on $[V(V)]_{total}$ and pH, additional V(V) hydrolysis products [10] [16–18]. The ^{17}O- and ^{51}V-NMR signals for these 'minor impurities' are largely assigned, especially in the pH and $[V_{10}]_{total}$ ranges of the present study. For our main goal, *viz.* a quantitative assessment of the exchange properties of decavanadate, it seems imperative to know the qualitative and quantitative composition of the solutions. These data are largely available from recent work on the decavanadate $\rightleftharpoons$ metavanadate equilibria, involving ^{51}V-NMR and potentiometric data [10].

The O-exchange properties of decavanadate have already been studied in some detail by ^{18}O-sampling techniques [9] [25] [26]. It was found that all structural types of O

exchange with an identical rate, *viz.* all O-atoms are kinetically identical. This surprising result was explained on the basis of a 'half-bonded intermediate' mechanism *(Fig. 1, b)* where the formation of the 'half-bonded intermediate' is rate-determining [9][2]). Clearly, even under these conditions, the seven types of O-atoms do not have to become kinetically *identical,* only *similar*. Since the ^{18}O-sampling technique only measures one amplitude (*viz.* the sum of all exchanging O-atoms), it does not allow to separate several reactions with similar rates. Since all seven signals in the ^{17}O-NMR spectra of decavanadate are cleanly resolved, a kinetic NMR study offers itself to clarify the remaining doubts. We, therefore, present our results of a ^{51}V- and ^{17}O-NMR study of aqueous decavanadate solutions.

Experimental. – *Chemicals and Solutions.* $Na_6V_{10}O_{28} \cdot 18\ H_2O$ was prepared according to [27]. Enriched water was from *Yeda R + D,* Rehovot, Israel (16.03% $^{17}OH_2$). Natural H_2O was doubly distilled and all other chemicals were of *puriss p.a.* or similar degrees. ^{17}O-enriched decavanadate was prepared by dissolving the $V_{10}O_{28}^{6-}$ salt (1.3769 g) in $^{17}OH_2$ (5.0173 g) and leaving it for *ca.* 60 h before freeze-drying the product. ^{17}O-NMR kinetic experiments were run either on enriched $V_{10}O_{28}^{6-}$ dissolved in buffered natural H_2O or on natural abundance $V_{10}O_{28}^{6-}$ dissolved in buffered $^{17}OH_2$. For one experiment, an unbuffered soln. was used. $[V_{10}]_{total}$ was generally *ca.* 0.17*m*. Because of the relatively high concentration of the substrate which was necessary for the ^{17}O-NMR measurements, and since the decavanadate system is complicated by numerous equilibria, no electrolyte was added. The ionic strength is, however, relatively constant in the whole series of measurements, since the $[V_{10}]_{total}$, which dominates the ionic strength, is held constant. The solns. were buffered with amine bases (aniline, pyridine, MES, collidine; [buffer base] $\approx 0.15m$), and the pH was adjusted with $HClO_4$. The pH was measured of equilibrated solns. The constance of pH of buffered solns. during the whole reaction period is clearly shown by the ^{17}O-NMR measurements (see *Results*).

^{17}O- and ^{51}V-NMR spectra were recorded at 54.261 MHz and 105.247 MHz, respectively, on a *Bruker AM 400* instrument which was equipped with a wide bore cryomagnet and with an *Aspect 3000* data system. The sweep width was 83 333 Hz or 50 000 Hz for ^{17}O- and ^{51}V-NMR spectra, respectively. The pulse length (PW) was 14.0 μs or 9.0 μs[3]); the aquisition time (AQ) was 0.02458 s or 0.04096 s; the FID was accumulated for 100 000 (50 000 for the first 20 spectra in kinetic runs and for the equilibria studies) or 1000 pulses, for ^{17}O- and ^{51}V-NMR spectra, respectively. An exponential line broadening function of 50 or 20 Hz was applied for ^{17}O-NMR spectra. The temp. was stabilized by blowing thermostated air through the NMR probe, and measured with a substitution technique [28]. Chemical shifts of ^{17}O-NMR signals are all *vs.* bulk H_2O at 0 ppm. For the ^{51}V-NMR spectra decavanadate is the reference (signal *1* is at −422 ppm; *vs.* $VOCl_3 = 0$ ppm, [18]).

pH Measurements were performed with a *Metrohm 605* pH-meter using a combined glass pH electrode calibrated by standard buffer solns. *UV/VIS Spectra* were recorded on a *Perkin Elmer Lambda 7* instrument. *Computations* (least-squares fits and O exchange simulations) have been performed on *Hewlett Packard 9000 Series 200* PC's in Basic 3.0.

Results. – The aim of the present study was to reinvestigate the O-exchange properties and mechanism of decavanadate in aqueous solution. Presently, ^{17}O-NMR spectroscopy is established as the most powerful technique for this type of problem. Before presenting and analyzing the O-exchange properties of decavanadate based on time-resolved ^{17}O-NMR data, we have to discuss some facts and data on which our analysis is based.

Various studies (*e.g.* pH studies including equilibrium and rapid-flow techniques [8] [10] [20–24], ^{18}O-labelling studies [9] [25] [26] and ^{51}V- and ^{17}O-NMR studies [10] [14–18]

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[2]) We note that the formation of the 'half-bonded intermediate' does not have to be rate-determining in this model, as was claimed in [9]. In fact, the reported kinetic parameters [9] indicate that O exchange at the intermediate and not its formation is rate-determining (note that this is in contrast to the results presented here).

[3]) The pulse width of 14 μs leads to a non-uniform distribution of excitation energy over the sweep width of 83 kHz. The effects on the integrals of resonances lying at the lower and higher ends were taken into account.

[29–33]) clearly indicate the presence of metavanadates in aqueous solutions of decavanadate. In the pH region of our studies, the metavanadates present may be assumed to be cyclic $(VO_3^-)_n$ species with $n = 4, 5$ *(Fig. 1)* [10] [29] [34–37]. All ^{17}O- and ^{51}V-NMR signals of decavanadate and metavanadates have been assigned [10] [18], and the assignements are in good agreement with expectations based on various metal-oxo ions [38] and with a recent ^{17}O-, ^{51}V-, and $^{17}O\{^{51}V\}$-NMR study [39].

The pH-, $[V(V)]_{total}$, and ionic-medium-dependent equilibria between various vanadates have been studied extensively [10]. To avoid any misinterpretation, we have remeasured the quantitative composition of aqueous solutions of decavanadate under the exact conditions of the O-exchange experiments (^{17}O- and ^{51}V-NMR spectroscopy, T and $[H^+]$ dependencies). These results, which are in good agreement with published data ($[V_{10}] \approx 0.17m$; $5 < pH < 5.5$; $278 < T < 313$ K, $V_4O_{12}^{4-}/V_5O_{15}^{5-} \sim 4:1$, $[(VO_3^-)_n]_{total} \approx 8\%$) are presented as *Supplementary Material.*

Of some importance for the interpretation of the O-exchange mechanism of decavanadate are kinetics and mechanism of the formation of metavanadates from decavanadate. Therefore, we now present these data[4]).

The Formation of Metavanadates from Decavanadate. The kinetics of the formation of metavanadates have been studied under the same conditions as the kinetics of the O-exchange reaction of decavanadate ($[V_{10}]_{total} \sim 0.17m$, pH ~ 5.55, $T = 298$ K). They have been followed by the measurement of the integral of the ^{17}O-NMR signal of the terminal O-atoms of the metavanadates (929 ppm) as a function of time (the O exchange of metavanadates is at least 100 times faster than their formation rate from decavanadate (see below)) and by the measurement of the pH of unbuffered decavanadate solutions as a function of time. The pH measurements have been run potentiometrically and by the measurement of the pH-dependent ^{17}O-NMR chemical shifts of decavanadate. On the basis of the analysis of the decavanadate $\rightleftharpoons$ metavanadate equilibria the formation of metavanadates is stoichiometrically well defined *(Eqn. 1)*.

$$8\ V_{10}O_{28}^{6-} + 16\ H_2O \rightleftarrows 15\ V_4O_{12}^{4-} + 4\ V_5O_{15}^{5-} + 32\ H^+ \quad (1)$$

However, the detailed reaction mechanism remains unknown. Nevertheless, a minimum of chemically reasonable assumptions allows a qualitative kinetic analysis of the reaction. Based on the relative stability of tetrameric cyclic metavanadates, on the suggested fragmentation pattern (see below), which is consistent with the observed sites of protonation (see *Discussion*) and with the observed O exchange pattern of decavanadate (see below), and based on the relative lability of metavanadates [9] (which is supported by the relatively fast O-exchange rate of metavanadates (see below)), the rate-determining step of the fragmentation process (*formation* of metavanadates) is the formation of a V_6 and a V_4 unit *(Fig. 1, c, Eqn. 2)*.

$$V_{10}O_{28}^{6-} + 3\ H_2O \rightleftarrows V_6O_{19}^{8-} + V_4O_{12}^{4-} + 6\ H^+ \quad (2)$$

The absence of any additional signals in the ^{51}V- and ^{17}O-NMR spectra attributable to the V_6 unit might suggest that this species is quite labile, *viz.* its steady-state concentration

[4]) There are earlier reports on kinetic studies of this reaction [40] [41]. Since these measurements are strongly media-dependent, they have been repeated under the same conditions as the O-exchange studies. No effort has been made, however, to elucidate the media dependence.

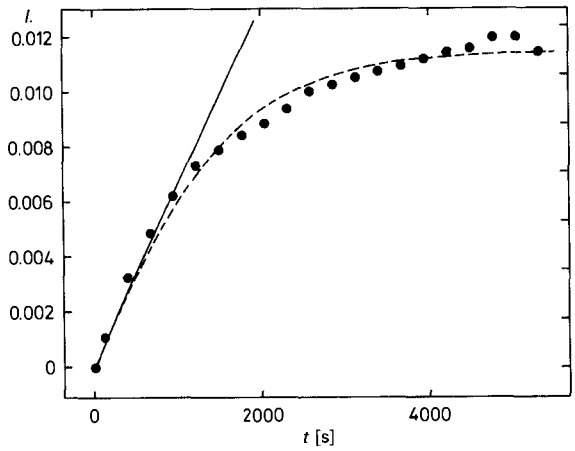

Fig. 2. *Kinetics of metavanadate formation followed by ^{17}O-NMR spectroscopy* (normalized integral of signal *T*). $T = 298$ K, pH = 5.60, $[V_{10}]_o = 0.1697m$. The full line is a fit to a first-order fragmentation reaction to completion ($k_1 = 4 \cdot 10^{-5}$ s^{-1}). The broken line is based on a fit leading to an equilibrium concentration of ~ 8% metavanadates and assuming a second-order back reaction (see text).

is very low, supporting the above considerations. The back reaction (formation of decavanadate from metavanadates, *Eqn. 1*) is a reaction of at least second-order. However, the exact reaction order, the nuclearity and structure, and the concentration of the species involved in the rate-determining step are not known. Our qualitative kinetic analysis of the formation of metavanadates from decavanadate is, therefore, based on v_0 kinetics (*i.e.* it is assumed that the reaction (first-order) goes to completion, and that the influence of the back reaction in the first few experimental points is minimal, *Fig. 2*). The resulting rate constant $k_1 \geqslant 4.0 \cdot 10^{-5}$ s^{-1}, based on the measurement of the ^{17}O-NMR integrals[5]), is subject to quite a large experimental error. This is due, apart from the rather crude kinetic analysis, to the fact that, at the start of the reaction, the concentration of metavanadates is very low indeed (error on integrals ~ 20%). Also shown in *Fig. 2* is a fit of the experimental points to a rate law based on a hypothetical mechanism of the type A $\rightleftarrows$ B + C (note that protons are omitted (buffered solution); B, C are metavanadates, second-order back reaction; rate law similar to *Eqn. 11*). Clearly, such an analysis is purely speculative. However, the resulting parameters, *viz.* the equilibrium concentration of metavanadates $[(VO_3^-)_n]_\infty \approx 8\%$ and the formation rate of metavanadates $k_1 \approx 4.0 \cdot 10^{-5}$ s^{-1} are in good agreement with the values deduced from the equilibrium studies and the v_0 kinetics, respectively.

O-Exchange Kinetics of Decavanadate. The O-exchange reaction of decavanadate with bulk H_2O has been studied by ^{17}O-NMR spectroscopy ($[V_{10}]_{total} \approx 0.17m$, pH ~ 5.55, $T = 298$ K). The experimental data which are shown in *Figs. 3* and *4* (*Tables* with experimental and fitted rate data are given as *Supplementary Material*) clearly indicate that the

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[5]) Since there is considerable uncertainty concerning the pK_a values of decavanadate [8] [10] [20–24] [34], which have to be considered in a kinetic analysis, only the results of the study based on ^{17}O-NMR integrals are presented in detail. It is, however, important to note that the data based on pH-studies are in qualitative agreement with the presented ones.

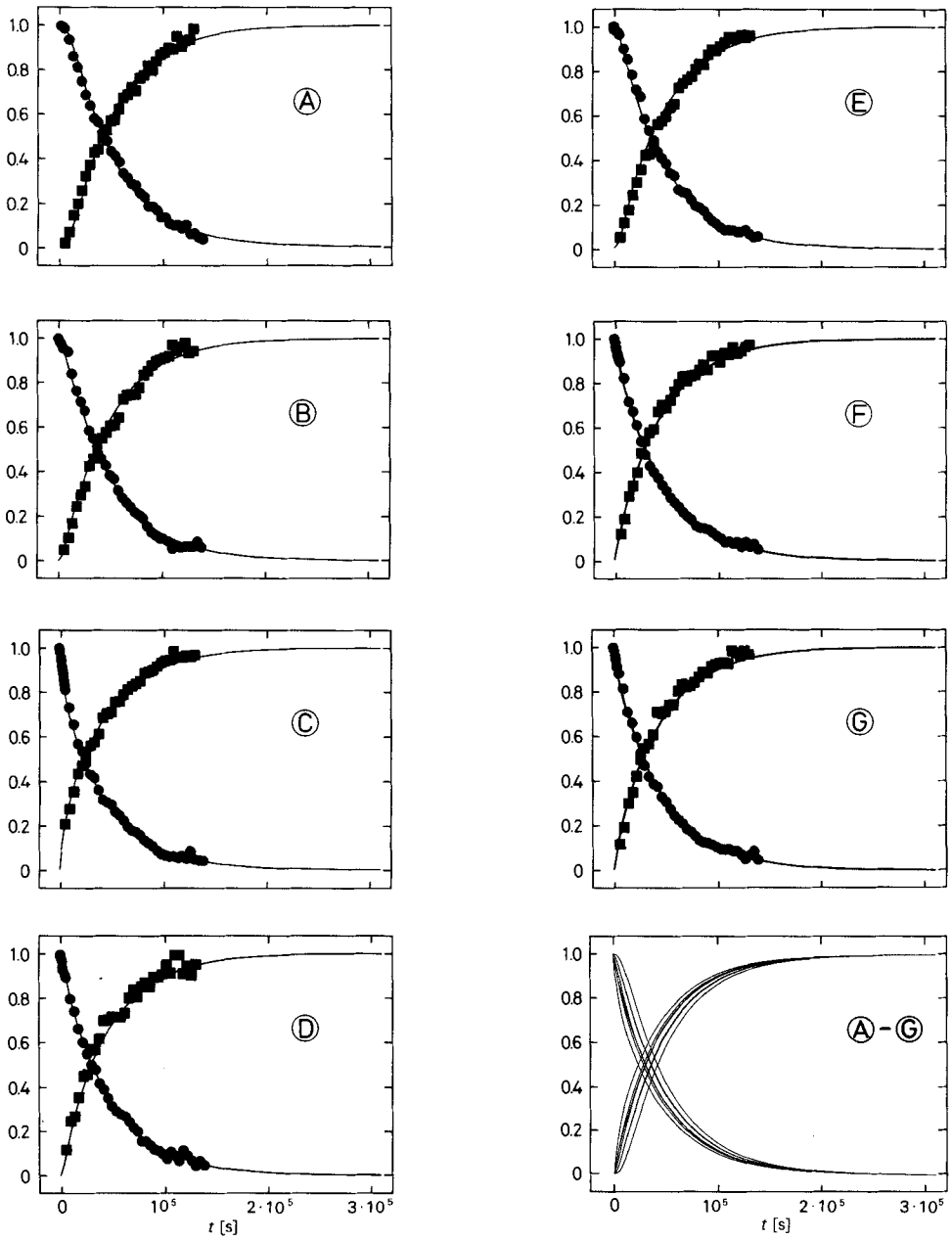

Fig. 3. *Kinetics of the O-exchange reaction of decavanadate with bulk H_2O.* The experimental points are corrected ^{17}O-NMR integrals and the full lines represent computer simulations based on the 'half-bonded-intermediate' mechanism (the structural site of the O-atoms (A–G) is indicated in each fit, for labels see *Fig. 1*; the plot in the bottom right corner shows the simulation of the exchange reaction of all seven structural sites). Two experiments (simulated with the same parameters, see *Table 2*) are shown: unlabelled $V_{10}O_{28}^{6-}$ in $H_2{}^{17}O$ (intensities increase with time) and $V_{10}{}^{17}O_{28}^{6-}$ in natural abundant H_2O (intensities decrease with time).

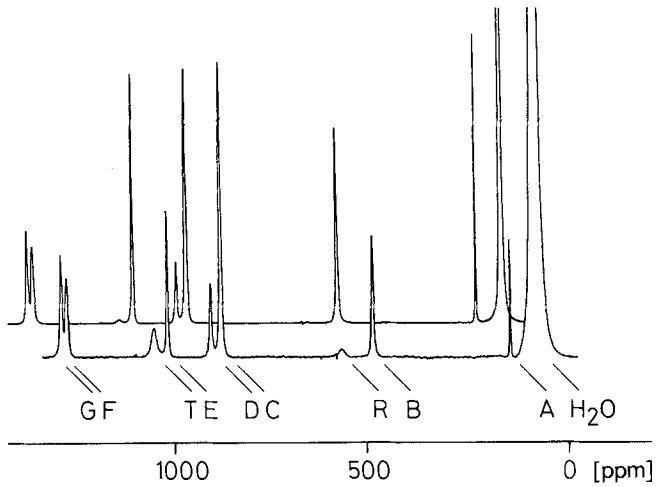

Fig. 4. *^{17}O-NMR spectra of decavanadate 11½ h after dissolution* ($[V_{10}]_{total} \sim 0.17m$, pH ~ 5.60, $T = 298$ K). *Top:* natural abundant H_2O/enriched $V_{10}{}^{17}O_{28}^{6-}$; *bottom:* enriched $H_2{}^{17}O$/natural abundant $V_{10}O_{28}^{6-}$.

exchange rates of the various O sites are *similar but not identical*. In the following, we present an analysis of the kinetic data based on these facts and published observations[6]).

A recent ^{18}O-exchange study on decavanadate has claimed that all seven structurally different types of O-atoms are kinetically equivalent [9] [25] [26]. Evidently, this is only possible when at least one intermediate allows the O-atoms to become structurally equivalent, and the published kinetic results have been discussed on the basis of a 'half-bonded intermediate' *(Fig. 1, b)*. Our kinetic results clearly establish that the structurally different O sites are *kinetically similar but not identical*. This implies that some O scrambling is involved. The proposed mechanism, based on a 'half-bonded intermediate', is but one possible route to allow the O sites to exchange. A completely 'open intermediate' *(Fig. 1, c)* seems to be a reasonable alternative. Clearly, activated intermediates resulting from other fragmentation sites than the ones, depicted in *Fig. 1, b* and *c*, might also be possible. However, on the basis of our kinetic results, and based on the decavanadate → metavanadate fragmentation processes and on the protonation sites of decavanadate (see *Discussion*), these other possibilities seem to be unrealistic, and they will not be further discussed. A mechanism based on a complete fragmentation of decavanadate into metavanadates (*i.e.* the V_6 unit in *Fig. 1 c* is further degredated) can be eliminated on the basis that it would lead to full scrambling, *viz.* all O sites would be kinetically identical. We have analyzed our ^{17}O-NMR kinetic results based on the models with a 'half-bonded' and a completely 'open' intermediate *(Fig. 1, b* and *c)*.

The general equation for O exchange of decavanadate with bulk H_2O is given in *Eqn. 3*, and the two hypothetical intermediates under scrutinity in this investigation are

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[6]) We stress that a thorough analysis would involve the investigation of pH, μ, T, counterion, and $[V_{10}]_{total}$ dependences, in addition to the results presented herein. Our restriction to *one* reaction medium clearly prevents a thorough analysis with respect to possible pre-equilibria and H^+ catalysis. However, earlier publications have dealt with these questions, and these results are integrated into our interpretations (see also *Discussion*).

given in *Eqns. 4* and *5*. With $V_{10}O_{28}^{6-}$, there are $\prod_{i=1}^{7}\binom{2+n_i-1}{n_i} = 50\,625$ differently labelled species in the system (i is the number of structurally different O-atoms in the isopolyanion, n_i is the total number of structurally identical O-atoms per site, *viz.* 2, 4, 8, 2, 4, 4, 4), *i.e.* $[V_{10}{}^*O_a^A\,O_{2-a}^A\,{}^*O_b^B\,O_{4-b}^B\,{}^*O_c^C\,O_{8-c}^C\,{}^*O_d^D\,O_{2-d}^D\,{}^*O_e^E\,O_{4-e}^E\,{}^*O_f^F\,O_{4-f}^F\,{}^*O_g^G\,O_{4-g}^G]^{6-}$.

$$\left.\begin{array}{l} \underbrace{V_{10}O_{28}^{6-} \overset{n\,H_2O}{\rightleftarrows} \text{intermediate I} + 2n\,H^+}_{\text{O scrambling } k_1,\,k_{-1} \qquad H_2O \left\uparrow\right\downarrow {}^{17}OH_2} \\ V_{10}{}^*O_{28}^{6-} \overset{n\,H_2O}{\rightleftarrows} \text{intermediate I}^* + 2n\,H^+ \end{array}\right\} \text{O exchange } k_2 \qquad (3)$$

$$V_{10}{}^*O_{28}^{6-} + 2\,H_2O \rightleftarrows V_4O_{11}{-}O{-}V_6O_{18}^{10-} + 4\,H^+ \qquad (4)$$

$$V_{10}O_{28}^{6-} + 3\,H_2O \rightleftarrows V_4O_{12}^{4-} + V_6O_{19}^{8-} + 6\,H^+ \qquad (5)$$

The concentration dependence of all seven different O-atoms of each of these labelled species is described by a differential equation derived from *Eqn. 3*. It clearly is inappropriate to set up this system of 354 375 equations and solve them analytically.

We, therefore, have chosen to analyze this kinetic system on the basis of an algorithm which is based on the statistical properties of the system and which includes the basic kinetic parameters of the reaction sequence, *viz.* k_1, k_{-1}, and k_2. In general, the system involves the following points:

1. A generation Q is an event of reversible formation of the intermediate I.
2. The reformation of the initial state leads to some O scrambling (*i.e.* exchange among structurally different sites). The rate of *O scrambling* is dependent on the model used and on the frequency of intermediate formation (k_1).
3. The *overall* O-exchange rate is dependent on the concentration of the intermediate I (k_1, k_{-1}, $[I]_o$, $[I]_\infty$) and on the number n of O-atoms exchanging per lifetime of the intermediate I ($n \propto k_2/k_{-1}$).
4. The *individual* O-exchange rate is dependent on the overall O-exchange rate and on the rate of O scrambling.
5. There is an additional normalization factor k' which adjusts the number of generations Q to real time (s). k' is related to the frequency of intermediate formation.

The kinetic system can now be separated in a *'scrambling'* part and an *'exchange'* part. It is important to point out that, based on the time resolution of our experiments, all O- and V-atoms are, for both models, assumed to be structurally and kinetically equivalent in the reactive V_4 moiety [9][7]). This has an impact on the exchange properties and for the 'open' intermediate model *(Fig. 1, c, Eqn. 5)* also on the scrambling properties. It, however, does not influence the scrambling in the 'half-bonded' model, since the V_4 moiety remains fixed to the parent V_6 moiety in this case.

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[7]) The calculated kinetic parameters indicate that this is a valuable assumption.

Table 1. *O Scrambling Characteristics of $V_{10}O_{28}^{6-}$ Based of the Models* b *('half-bonded') and* c *('open' intermediate)*

Scrambling characteristics				
	1/4	1/2	1/4	
'Half-bonded'	1 A/E 2 B/C 1 D/E 1 G/E	1 A/B 1 B/C 1 B/E 1 C/E 1 C/D 1 E/F 1 F/G	no scrambling	
	1/6	2/3	1/12	1/12
'Open'	1 A/E 2 B/C 1 D/E 1 G/E	1 A/B 1 B/C 1 B/E 1 C/E 1 C/D 1 E/F 1 F/G	1 A/D 1 E/G 4 C/B	no scrambling

Scrambling characteristics based on the equivalency of O-atoms in the reactive intermediate (for model *c* only)	
	C = 13/18 C + 1/18 D + 2/18 F + 2/18 G D = 4/18 C + 10/18 D + 2/18 F + 2/18 G F = 4/18 C + 1/18 D + 11/18 F + 2/18 G G = 4/18 C + 1/18 D + 2/18 F + 11/18 G

Resulting generation-wise scrambling pattern	
'Half-bonded' intermediate (*b*)	A = 5/8 A + 1/4 B + 1/8 E B = 1/8 A + 1/2 B + 1/4 C + 1/8 E C = 1/8 B + 3/4 C + 1/16 D + 1/16 E D = 1/4 C + 5/8 D + 1/8 E E = 1/16 A + 1/8 B + 1/8 C + 1/16 D + 7/16 E + 1/8 F + 1/16 G F = 1/8 E + 3/4 F + 1/8 G G = 1/16 E + 1/8 F + 13/16 G
'Open' intermediate (*c*)	A = 13/24 A + 1/3 B + 1/108 C + 5/126 D + 1/12 E + 1/216 F + 1/216 G B = 1/6 A + 1/3 B + 13/54 C + 1/54 D + 1/6 E + 1/27 F + 1/27 G C = 1/6 B + 1/12 C + 1/12 D + 1/12 E + 1/12 F + 1/12 G D = 1/24 A + 13/36 C + 23/72 D + 1/12 E + 7/72 F + 7/72 G E = 1/24 A + 1/6 B + 5/27 C + 5/108 D + 1/3 E + 29/216 F + 5/54 G F = 5/27 C + 5/108 D + 1/6 E + 23/54 F + 19/108 G G = 11/54 C + 11/216 D + 1/12 E + 5/27 F + 103/216 G

The scrambling patterns, *viz.* the generation wise changes of occupancy for each O site for the 'half-bonded' and the 'open' intermediate models are given in *Table 1*. They are based on the probabilities for the intermediate formation (four and two equivalent possibilities for the 'half-bonded' and the 'open' intermediate, respectively) and the respective probabilities for the recombination reaction (four and twelve possibilities).

The O exchange in the reactive intermediate is for both models limited to the exchange of O-atoms of the structural types C, D, F, and G. Under the condition of equivalent exchange reactivity, of all nine O-atoms in the V_4 moiety the generation wise exchange is described by *Eqns. 6–9*, where $[X^*]_Q$ is the concentration of already exchanged O-atoms in generation Q and $[I]_Q$ is the corresponding concentration of the reactive intermediate.

$$[C^*]_m = [C^*]_{m-1} + 4/9\, n\,(1 - [C^*]_{m-1})\,[I]_m \quad (6)$$

$$[D^*]_m = [D^*]_{m-1} + 1/9\, n\,(1 - [D^*]_{m-1})\,[I]_m \quad (7)$$

$$[F^*]_m = [F^*]_{m-1} + 2/9\, n\,(1 - [F^*]_{m-1})\,[I]_m \quad (8)$$

$$[G^*]_m = [G^*]_{m-1} + 2/9\, n\,(1 - [G^*]_{m-1})\,[I]_m \quad (9)$$

The time dependence of $[I]_Q$ is described by the two integrated rate laws which describe the two reversible systems $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I$ (*Eqn. 10*) and $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I + B$ ($[I]_o = [B]_o = 0$; *Eqn. 11*) for the 'half-bonded' and 'open' models, respectively.

$$[I] = [A]_o - \exp\left(-\frac{k_1 t\,[A]_o}{[A]_o - [A]_\infty}\right)([A]_o - [A]_\infty) + [A]_\infty \quad (10)$$

$$[I] = [A]_o - \frac{\exp\left(k_1 t \dfrac{[A]_o + [A]_\infty}{[A]_o - [A]_\infty}\right)[A]_o[A]_\infty + [A]_o^2}{[A]_\infty + [A]_o \exp\left(k_1 t \dfrac{[A]_o + [A]_\infty}{[A]_o - [A]_\infty}\right)} \quad (11)$$

The time t is given by the already mentioned normalization function $t = Q/k'$, where $k' = k_1$. The time-dependent ^{17}O-NMR data (the integrals had to be corrected with the calculated or directly measured values for $t = 0$ and $t = \infty$, and normalized to a scale from 0 to 1) could now be fitted to a simulation of the reaction which involves the reversible formation of the intermediate *(Eqn. 10* or *11)*, the O exchange *(Eqns. 6–9)* and the O scrambling *(Table 1)*. The fitted parameters contain all kinetically relevant parameters of the system, *viz.* k_1, k_{-1}, $[I]_o$ and $[I]_\infty$ (describing the formation of the reactive intermediate I) and n (which is related to the rate of O exchange k_2).

The experimental data *(Fig. 3)* clearly show that there is an albeit small kinetic difference within the various O sites of decavanadate. This implies some O scrambling at an intermediate state. The non-equivalence is also evident, if one compares identical reactions starting with labelled (decrease of the signals) and unlabelled (increase of the signals) decavanadate *(Fig. 4)*.

The simulations of the O-exchange reaction of decavanadate based on the 'half-bonded-intermediate' mechanism are presented in *Fig. 3*, and the calculated parameters are given in *Table 2*. A simulation based on the 'open-intermediate' mechanism gives kinetic parameters which are not consistent with the qualitative results of the kinetics of the formation and the equilibrium concentration of the decavanadate – metavanadate reaction (see above), *viz.* for a good fit the formation rate of metavanadates is about 100 times faster than the measured rate ($k_1 \approx 1.5 \cdot 10^{-3}\ s^{-1}$ *vs.* $k_1 \approx 4.0 \cdot 10^{-5}\ s^{-1}$). Moreover, the equilibrium concentration of metavanadates required for a good fit is by a factor of ~ 2 too large (see *Discussion*).

Table 2. *Kinetic and Thermodynamic Parameters for the O-Exchange Reaction of Decavanadate Deduced from the Simulation Based on a 'Half-bonded Intermediate'* (for structures and stoichiometries see *Fig. 1* and *Eqns. 3* and *4*)

$k_1 = 5.8 \cdot 10^{-3}\ s^{-1}$	$[V_{10}]_\infty = 0.1562m$	$\tau^a) = 14.9$ s
$k_{-1} = 6.7 \cdot 10^{-2}\ s^{-1}$	$[\text{intermediate}]_\infty = 0.0135m$	$N^b) \geq 9$
$K' = 0.086$		

a) Lifetime of the intermediate state. b) Number of O exchanges per generation.

Discussion. – The solution structure of decavanadate was shown by ^{17}O- and ^{51}V-NMR spectroscopy to be qualitatively identical with its well known solid state structure [13] [18], *viz.* there are seven structurally different types of O sites *(Fig. 1)*. If the O exchange with bulk H_2O were on this condensed structure, one would expect enormous differences in the exchange rates of the various types of O-atoms (*e.g.* the terminal O-atoms and the μ_2- and μ_3-oxo bridges might exchange, although the exchange rates can be expected to be rather slow [38]; the central O-atoms (A), however, are essentially blocked against exchange with bulk H_2O). Since the rates are similar, it follows unambiguously that the O-exchange reaction must involve an activated intermediate. Whether the intermediate is of the general type of the V_4–V_6 fragmentation product shown in *Fig. 1* or not (for different possibilities, see *Results*), some V—O bonds have to be cleaved. The question of the site of fragmentation, and, therefore, the structural type of the activated intermediate, might be related to the sites of protonation of decavanadate in aqueous solution, *viz.* the fragmentation might be H^+-catalyzed. Therefore, we first turn to the question of protonation of $V_{10}O_{28}^{6-}$.

The pK_a values of decavanadate are in the ranges of $pK_a^1 = 5.5$–6, $pK_a^2 = 3.1$–3.7, $pK_a^3 \approx 2$ [8] [10] [14] [20–24]. Therefore, the pH region of our experiments (pH ~ 5–5.5) corresponds approximately to a single protonation of $V_{10}O_{28}^{6-}$. There still is considerable argument about the sites of protonation. In various analyses, based on chemical intuition [34] [44], X-ray data [12–14] [42] [45], bond length – bond number calculations [46], calculations of covalent bond strenghts [47], ^{17}O- and ^{51}V-NMR spectroscopy [14] [17] [43], the site of deprotonation has been assumed at terminal (F and G), doubly bridged (C), and triply bridged (B) sites. Some inconsistencies and misinterpretations are due to the fact that X-ray data are not necessarily relevant for solution studies, *i.e.* a particular protonation pattern might be stabilized by H-bonding or the crystallized species might accidentally be the least soluble of a variety of isomers. On the other hand, the interpretations of the ^{17}O- and ^{51}V-NMR solution studies are limited by the fact that the structural changes which result upon protonation have not been accounted for in the earlier studies. Clearly, the change of electron density around an O-atom, which is largely responsible for the observed spectral changes, is not only a result of the protonation of a distinct O site, but also of overall structural changes resulting from this protonation. These aspects have been acknowledged in a recent study, based on X-ray data, ^{17}O- and ^{51}V-NMR spectroscopy, and vapour-pressure osmometry, leading to the triply bridged sites B and the doubly bridged sites C as the preferentially protonated O-atoms of decavanadate [14]. Our kinetic results which are based on V_3—O_B, V_2—O_D, and V_2—O_E bond cleavage might suggest that O B sites are preferentially protonated. However, one has to distinguish between *the most basic O sites* and *the most reactive conjugate acid* which *do not have to be identical.*

Published data demonstrate that the rate of O exchange of decavanadate with bulk H_2O is nearly constant in the pH range of 4.0–6.3, increases below pH ~ 4.0, and decreases above pH ~ 6.3 [9]. This is consistent with the hypothesis that protonation of $V_{10}O_{28}^{6-}$ assists the fragmentation which leads to the activated intermediate ($pK_a^1 \approx 5.5$–6.0, $pK_a^2 \approx 3.1$–3.7 [8] [10] [20–24]; note that the pH dependence of the equilibria which lead to the activated intermediate *(Eqns. 4* and *5)* as well as protonation of the intermediate itself would also have to be considered in a quantitative analysis of the data).

We now turn to the kinetics of the O-exchange reaction of decavanadate *(Fig. 3)*. The overall O-exchange rate is dependent on the frequency of formation of the activated intermediate I and on the number of O-atoms exchanging per lifetime of the intermediate, which is related to the exchange rate of the intermediate and its steady state concentration. The rate differences of the various geometrical sites are largely governed by the scrambling rate and mechanism. This is most clearly visible at the initiation state of the O-exchange reaction (see *Fig. 3*). There are two sets of O sites, *viz.* A, B, E (relatively slow exchange), and C, D, F, G (relatively fast exchange), respectively. This clearly supports the structural type of the intermediate envisaged *(Fig. 1, c* and *d)*, where O-atoms C, D, F, and G are the exchange sites. Qualitatively the same result was recently reported for $H_3V_{10}O_{28}^{3-}$ which was 'selectively enriched' at sites C, D, F, and G [14].

In principle, qualitatively similar simulations of the exchange reaction based on both models considered ('half-bonded' and 'open') may be obtained (for the 'half-bonded' intermediate, see *Fig. 3* and *Table 2*). This is not unexpected, since the scrambling pattern for both models is rather similar (see above and *Table 1*). A differentiation of the two models based on the goodness of fit does not seem to be reasonable in view of the great number of parameters to fit and on the quality of the measured data (error on integrals of $\sim \pm 10\%$). The parameters obtained for the best fit based on the 'open-intermediate' model, however, indicate that O exchange resulting from metavanadate intermediates alone cannot be responsible for the observed exchange pattern (see *Results* and below).

An important difference of any 'half-bonded' mechanism (independent of the fragmentation sites) compared with any 'open' mechanism (where decavanadate is degredated into two or more (metavanadate) fragments; a 'completely degredated' intermediate can be ruled out, see *Results*) is the fact that the former are unimolecular and the latter at least bimolecular processes. Therefore, based on a mechanism with a fragmented intermediate, the kinetics of the O-exchange reaction are expected to be strongly dependent on $[V_{10}]_{total}$ and on $[H^+]$ (based on the $[H^+]$ dependence of the decavanadate $\rightleftharpoons$ metavanadate equilibrium; *Eqn. 1*). This does not seem to be the case in the pH range of $4 \leqslant pH \leqslant 6.3$ [9]. However, one has to be careful in a quantitative interpretation of these results. *i)* The ionic strength is strongly dependent on $[V_{10}O_{28}^{6-}]$ and not held constant. *ii)* The conditions of the kinetic experiments are approaching pseudo-first-order, *viz.* there is an approximately 10-fold excess of decavanadate under the conditions of our experiments. However, the decavanadate/metavanadate ratio might be shifted towards a higher metavanadate fraction under the conditions of the earlier ^{18}O-exchange study [9]. The $[V_{10}]_{total}$ of the present investigation is roughly 10 times larger than that of the earlier work, whereas the overall O-exchange rate of decavanadate is only about doubled ('$t_{1/2}$' $\sim$ 15 h [9] *vs.* $\sim$ 7 h).

An additional result of interest comes from pressure-dependent kinetics of the O-exchange reaction of decavanadate [9]. The resulting small negative volume of activation clearly supports the exchange mechanism based on a 'half-bonded' intermediate, and, on a qualitative basis, it is not consistent with an exchange mechanism based on activated intermediates resulting from fragmentation of decavanadate.

Three points, which emerge from the analysis of our data, need some further discussion: *i)* according to our analysis, the formation rate of metavanadates ($k_1 \approx 4 \cdot 10^{-5}\,s^{-1}$) is about two orders of magnitude slower than the formation of the structurally similar

'half-bonded' intermediate ($k_1 \approx 6 \cdot 10^{-3}$ s^{-1}). *ii)* The equilibrium concentration of metavanadates and the 'half-bonded' intermediate are similar ($\sim 8\%$). The back reaction (formation of decavanadate from the intermediates) is, therefore, considerably faster in the 'half-bonded' intermediate. *iii)* Whereas metavanadates are easily detected by ^{17}O- and ^{51}V-NMR spectroscopy, the 'half-bonded' intermediate, which has a similar concentration, is not.

We first concentrate on the kinetic aspects. The fragmentation processes leading to the 'half-bonded' intermediate and to metavanadates (*via* the 'open' intermediate) are chemically very similar. The formation of metavanadates is clearly favored in terms of entropy, whereas the smaller order of V–O bond-cleavage, the high ionic strength and the smaller amount of charge separation might favor the formation of the 'half-bonded' intermediate. Therefore, a quantitative expectation of the ratio of the two formation rates is clearly not warranted, *viz.* the rate difference is not unexpected. Furthermore, in a quantitative assessment, the accuracy of the two rates has to be remembered (the formation rate of metavanadates results from a relatively crude analysis and is only well defined as a lower limit). However, the difference of more than two orders of magnitude indicates that the formation of metavanadates is significantly slower than the formation of the 'half-bonded' intermediate. The similarity of the O-exchange rates of the various geometrical sites together with the number and interdependences of parameters in the simulation of the O-exchange reaction indicates, that the errors of these parameters might also be substantial. However, the kinetic parameters are supported by a fit which clearly is of good quality *(Fig. 3)* and by the fact that the O-exchange rate of the 'half-bonded' intermediate $k_2 \geqslant 0.6$ s^{-1} (calculated from the kinetic parameters, see *Table 2*) is as expected from earlier measurements ($k_2 \approx 0.5$ s^{-1}) [9]. The back reaction (formation of decavanadates from the two types of intermediates) is, as expected, faster for the 'half-bonded' intermediate. We now turn to the question, why the 'half-bonded' intermediate remains undetected by NMR spectroscopy, whereas metavanadates of similar concentration are clearly observed. The main reason is the relative asymmetry of the species. The assumed structure of the 'half-bonded' intermediate *(Fig. 1)* reveales that seven structurally different V and fourteen O sites exist. The calculated intensities of the expected NMR signals are, therefore, 2 to 20 times lower than the signals for decavanadate and metavanadates. Moreover, the structural differences of the various O and V sites of the 'half-bonded' intermediate are very small. The signals are, therefore, expected to the 'ill-resolved' and quite broad and, given the structural similarity to decavanadate and metavanadate species, partially obscured by other signals. Furthermore, given the uncertainty on the kinetic parameters, the error limit on the concentration of the intermediate might be quite large as well.

Clearly, some contribution to the O exchange of decavanadate from an 'open' intermediate cannot be ruled out. Based on our kinetic analysis (similar concentration of intermediates, all O-atoms of the respective intermediate exchange per lifetime), the rate difference of the two mechanisms for O exchange of decavanadate is largely governed by the rate difference of the intermediate formation. A possible contribution of O exchange of decavanadate by an 'open' intermediate mechanism is, therefore, of the order of 1–2% at most.

We conclude that, under the present conditions ($[V_{10}]_{total} \approx 0.17m$, pH ≈ 5.5, $T = 298$ K), the seven structurally different O sites of decavanadate are kinetically similar but not

identical. Although the kinetic analysis is not exhaustive (*e.g.* μ, $[V_{10}]_{total}$, counterion, T and pH dependences have not been reinvestigated thoroughly[6]), the present results are fully consistent with an exchange mechanism based on the formation of a 'half-bonded' intermediate.

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Supplementary Material Available. [H^+]- and T-dependent ^{17}O- and ^{51}V-NMR data of solns. of decavanadate *(Table S1, Fig. S1)* and experimental data and simulations (numerical data) of the O-exchange reaction of decavanadate *(Table S2)*.

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