Transient Intermediates in the Polymerisation of Tungstate

By **David L. Kepert** * and **James H. Kyle**, The University of Western Australia, Nedlands, W.A. 6009, Australia

The reaction of alkaline solutions of $Na_2[WO_4]$ (*ca.* 10^{-3} mol dm^{-3}) with acid has been studied by stopped-flow-spectrophotometric and indicator-spectrophotometric techniques. The formation of 'acid paratungstate', $[H_8W_6O_{24}]^{4-}$, has been detected. It is the most important of the transient intermediates formed *ca.* 500 ms after mixing, before decomposition to a mixture of $[HW_6O_{21}]^{5-}$ and $[(HW_6O_{20})_n]^{3n-}$. It is confirmed that this 'acid paratungstate' exists for some hours in tetramethylammonium chloride solution.

ACIDIFICATION of tungstate(2—) solution leads to the rapid formation of isopolytungstates,[1] the most important being hydrogenhexatungstate(5—), $[HW_6O_{21}]^{5-}$, and poly[hydrogenhexatungstate(3—)], $[(HW_6O_{20})_n]^{3n-}$.

$$6[WO_4]^{2-} + 7H^+ \longrightarrow [HW_6O_{21}]^{5-} + 3H_2O \qquad (1)$$

$$6n[WO_4]^{2-} + 9nH^+ \longrightarrow [(HW_6O_{20})_n]^{3n-} + 4nH_2O \qquad (2)$$

Subsequent reactions to give dihydrogendodecatungstate(10—), $[H_2W_{12}O_{42}]^{10-}$, and dihydrogendodecatungstate(6—), $[H_2W_{12}O_{40}]^{6-}$, occur more slowly and equilibrium is not established even after several days. The most recent[2] potentiometric results obtained up to acid : tungstate (H : W) ratios of 7 : 6 have been interpreted as showing significant quantities of H_2WO_4, $[W_6O_{21}]^{6-}$, $[HW_6O_{21}]^{5-}$, and $[W_{12}O_{41}]^{10-}$; the relation between the last ion, which was formed 'almost instantaneously,' and $[H_2W_{12}O_{42}]^{10-}$ is unclear. At higher degrees of acidity, H : W = 1.6 : 1, decatungstate(4—), $[W_{10}O_{32}]^{4-}$, is formed.[3]

This work has usually been carried out using sodium tetraoxotungstate(VI) solutions. More recently, Le Meur and Souchay[4] studied the same reaction using tetramethylammonium ion as the supporting cation, and found that the product first detected was not any of the above ions, but was the 'acid paratungstate' ion which required 8 mol of acid per 6 mol of tungstate. This 'acid paratungstate' then decomposed to $[HW_6O_{21}]^{5-}$ and $[(HW_6O_{20})_n]^{3n-}$ with a half-time of some hours. We now report a stopped-flow study in which the pH and u.v. spectrum are recorded as a

---

[1] D. L. Kepert, 'The Early Transition Metals,' Academic Press, London, 1972; P. Souchay, 'Ions Mineraux Condenses,' Masson, Paris, 1969.

[2] Y. Sasaki, *Acta Chem. Scand.*, 1961, **15**, 175; R. Arnek and Y. Sasaki, *ibid.*, 1974, **A28**, 20.

[3] O. Glemser, W. Holznagel, W. Holtje, and E. Schwarzmann, *Z. Naturforsch*, 1965, **B20**, 725; J. Fuchs, H. Hartl, W. Schiller, and U. Gerlach, *Acta Cryst.*, 1976, **B32**, 740.

[4] B. Le Meur and P. Souchay, *Rev. Chim. minérale*, 1972, **9**, 501.

function of time. It is shown that the reaction of $[WO_4]^{2-}$ (*ca.* 10^{-3} mol dm^{-3}) with acid in the presence of sodium ions also forms 'acid paratungstate,' with decomposition to $[HW_6O_{21}]^{5-}$ and $[(HW_6O_{20})_n]^{3n-}$ taking *ca.* 1—60 s. Previous work includes an indicator–stopped-flow study at higher concentrations where the reaction is complicated by the formation of colloidal hydrated tungsten oxides,[5] and a continuous-flow potentiometric study.[6]

EXPERIMENTAL

Sodium tetraoxotungstate(VI), sodium hydroxide, and perchloric acid were analytical grade and used without further purification. Sodium tetraoxotungstate(VI) solutions were adjusted to pH 9 before use. Sodium perchlorate (analytical grade) was recrystallised from water and dried *in vacuo* before use as $Na[ClO_4]\cdot H_2O$. Tetramethylammonium chloride (B.D.H.) solutions were boiled with activated charcoal to remove the yellow colour.[7] Perchloric acid and $[NMe_4]Cl$ were standardised before use.[8] Bromocresol Purple and Bromocresol Green (B.D.H.) solutions were prepared and their pK determined as before.[5] Measurements were carried out on a modified [9] Durrum–Gibson stopped-flow spectrophotometer, and a Perkin-Elmer 450 spectrophotometer.

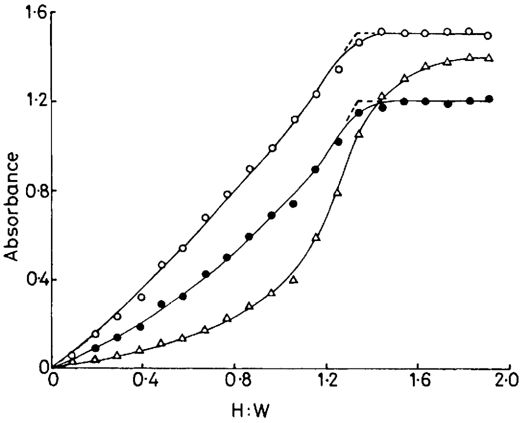

FIGURE 1 Spectrophotometric-titration curves of absorbance at 280 nm against the H : W ratio. $c_w = 5.33 \times 10^{-4}$ mol dm^{-3}, $I = 0.10$ mol dm^{-3} $Na[ClO_4]$, 25.0 °C. Products: (●) (1), (○) (2), and (△) (3)

RESULTS

Spectrophotometric-titration Curves.—The reaction following the addition of $HClO_4$ to an alkaline solution of $Na_2[WO_4]$ was followed at 280—310 nm at total tungstate (c_w) concentrations ranging from 5.33×10^{-4} to 2.06×10^{-3} mol dm^{-3}, and H : W ratios ranging from 0.0 to 2.0 : 1, with the ionic strength I maintained at 0.1 mol dm^{-3} with $Na[ClO_4]$. The spectral change occurred in three distinct stages: stage (1), a very rapid increase in absorbance which was complete within the mixing time (*ca.* 2 ms); stage (2), a further increase in absorbance, complete within 500 ms; stage (3), a slow decrease in absorbance, requiring from *ca.* 1—60 s for completion depending on the H : W ratio used. Further changes occurred over several days, but were not investigated.

Spectrophotometric-titration curves were obtained by plotting the absorbance at the end of each stage against the H : W ratio, typical curves being shown in Figures 1 and 2 for $c_w = 5.33 \times 10^{-4}$ and 2.06×10^{-3} mol dm^{-3} respectively. Very similar curves were obtained at intermediate concentrations.[10] In each case there is an end-point at H : W = 1.3_3 : 1 for the end of stages (1) and (2), and the curves corresponding to the end of stage (3) show a broad inflection over H : W *ca.* 1.0—1.5 : 1. Over this concentration range the solutions obey the Bouger–Beer law within experimental error.

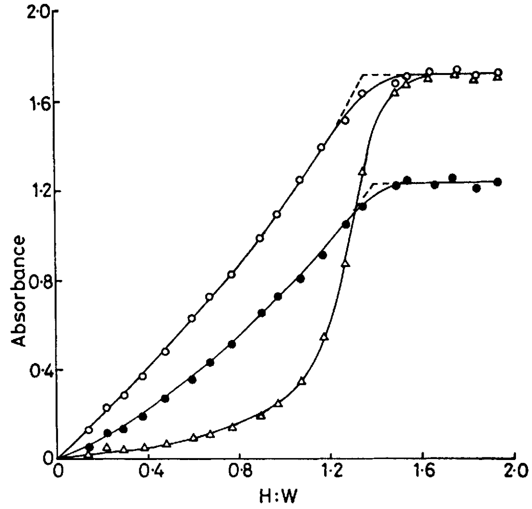

FIGURE 2 Spectrophotometric-titration curves of absorbance at 310 nm against the H : W ratio. $c_w = 2.06 \times 10^{-3}$ mol dm^{-3}, $I = 0.10$ mol dm^{-3} $Na[ClO_4]$, 25.0 °C. Products as in Figure 1

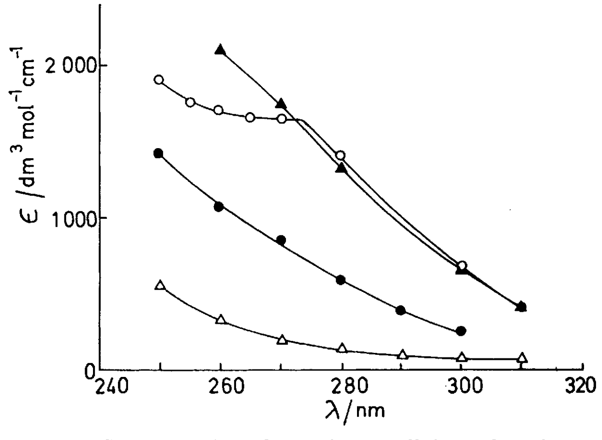

FIGURE 3 Spectra, with absorption coefficients based on c_w: (●) product (1), H : W > 1.3; (○) product (2), H : W > 1.3; (△) product (3), H : W < 0.5; (▲) product (3), H : W > 1.6 : 1

The spectrum at the end of stage (3) for H : W < 0.5 is identical to that of $[HW_6O_{21}]^{5-}$,[11] and that for H : W > 1.6

---

[5] J. C. Dewan and D. L. Kepert, *J.C.S. Dalton*, 1973, 224.

[6] G. Schwarzenbach and J. Meier, *J. Inorg. Nuclear Chem.*, 1958, **8**, 302; G. Schwarzenbach, G. Geier, and J. Littler, *Helv. Chim. Acta*, 1962, **45**, 2601.

[7] A. I. Vogel, 'A Text-book of Practical Organic Chemistry,' Longmans, London, 1956.

[8] A. I. Vogel, 'A Text-book of Quantitative Inorganic Analysis,' Longmans, 1962.

[9] B. W. Clare, D. L. Kepert, and D. W. Watts, *J.C.S. Dalton*, 1973, 2476.

[10] J. H. Kyle, Ph.D. Thesis, University of Western Australia, 1976.

is identical to the spectrum of $[(HW_6O_{20})_n]^{3n-}$,[11] the spectra at intermediate acidities corresponding to a mixture of these ions (Figure 3). The spectrum at the end of stage (2) (Figure 3) at H : W > 1.33 : 1 is the same as that of ' acid paratungstate ' reported by Le Meur and Souchay,[4] and of a solution of ' acid paratungstate ' prepared in 3.0 mol dm^{-3} $[NMe_4]Cl$ according to these workers. Accordingly the titration curves of Le Meur and Souchay were repeated. Measurements were made *ca.* 5 min after mixing, and remained unchanged for *ca.* 30 min. A typical titration curve is shown in Figure 4, and is very similar to the titration curves in $Na[ClO_4]$ at the end of stage (2) (Figures 1 and 2). These titration results indicate that ' acid paratungstate ' is the most important species initially formed under these conditions, but the significant curvature also indicates some formation of a less strongly absorbing species requiring a lower H : W ratio.

It is not possible to make any inferences as to the nature of the products at the end of stage (1) from the spectrum (Figure 3), although the spectrophotometric-titration curves at the end of stages (1) and (2) are very similar in shape (Figures 1 and 2).

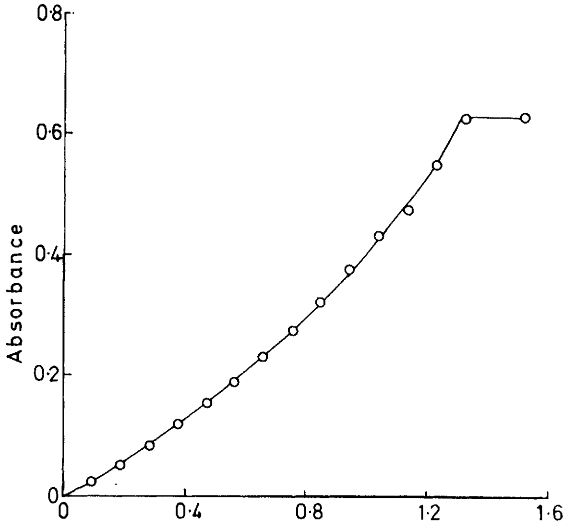

FIGURE 4 Spectrophotometric-titration curve of absorbance at 280 nm against the H : W ratio. c_w = 2.00 × 10^{-3} mol dm^{-3}, I = 3.00 mol dm^{-3} $[NMe_4]Cl$, 25.0 °C

Kinetic Studies.—The stopped-flow traces obtained for the spectrophotometric-titration curves also yield kinetic information for the formation [stage (2)] and decomposition [stage (3)] of ' acid paratungstate.'

The results for the first reaction were reproducible from run to run and gave good first-order rate plots (standard errors of ±1% in the rate constants, k_a). However, rate constants obtained from day to day were only reproducible to ±10%. In the region H : W > 1.25 : 1 the rate plots were slightly curved over the first *ca.* 20 ms, indicating the existence of other reactions. The observed rate constants (Figure 5) did not vary greatly with conditions, but reached a maximum at H : W *ca.* 0.7 and a minimum at *ca.* 1.5 : 1, and slightly increased with increasing c_w.

The results for the decomposition of ' acid paratungstate ' were again reproducible and yielded good first-order rate constants (standard error ±1%). Reproducibility from day to day was within ±5%. The rate constants reached a minimum at H : W *ca.* 1.1 : 1, and then increased sharply (Figure 6).

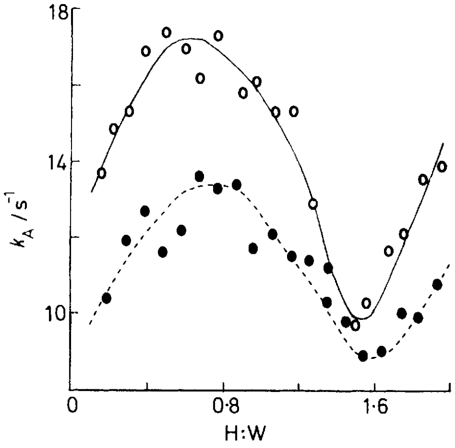

FIGURE 5 Observed first-order rate constants for the formation of product (2) as a function of the H : W ratio at I = 0.10 mol dm^{-3} $Na[ClO_4]$ and 25.0 °C. c_w = 5.33 × 10^{-4} (●) and 2.06 × 10^{-3} mol dm^{-3} (○)

pH-*Titration Curves.*—The rapid pH changes occurring on the addition of acid to alkaline $Na_2[WO_4]$ (c_W = 0.5 × 10^{-3}—2.0 × 10^{-3} mol dm^{-3} with $Na[ClO_4]$) were measured at 590 and 615 nm using Bromocresol Purple and Bromocresol Green indicators respectively.

The same three distinct stages in the reaction observed in the spectrophotometric study again occurred. Initially there was a very rapid increase in pH which was complete within the mixing time (*ca.* 2 ms), corresponding to the end of stage (1). The pH-titration curves (Figure 7) have a

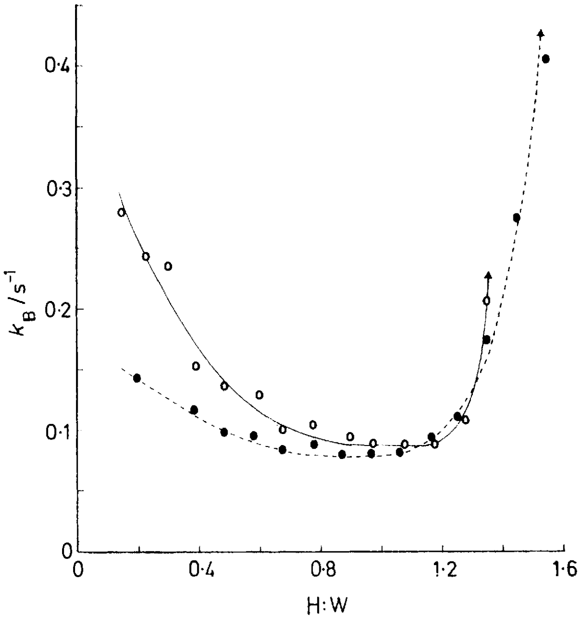

FIGURE 6 Observed first-order rate constants for the decay of product (2) as a function of the H : W ratio at I = 0.10 mol dm^{-3} $Na[ClO_4]$ and 25.0 °C. c_w as in Figure 5

---

[11] B. Le Meur and F. Chauveau, *Bull. Soc. chim. France*, 1970, 3834.

very broad end-point, indicating either that the product is a weak acid or that a number of products are formed with end-points extending over the region H : W *ca.* 1.0—1.5 : 1.

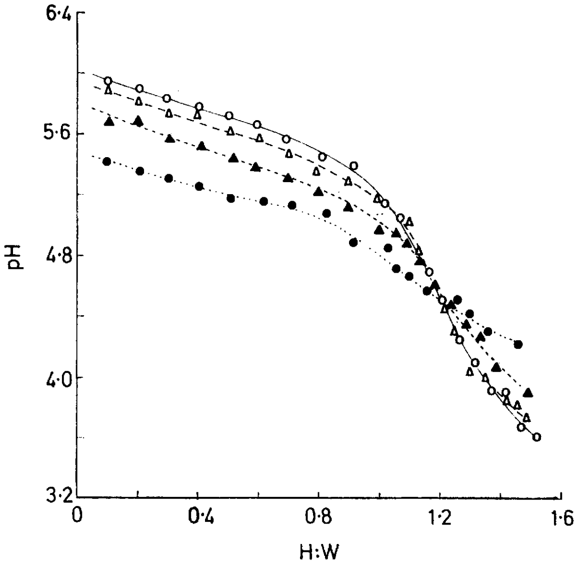

FIGURE 7 pH-Titration curves for the completion of stage (1) at I = 0.10 mol dm^{-3} Na[ClO$_4$] and 25.0 °C. c_w = 2.00 × 10^{-3} (○), 1.50 × 10^{-3} (△), 1.00 × 10^{-3} (▲), and 5.00 × 10^{-4} mol dm^{-3} (●)

The product or products cannot be simple protonated monotungstates such as $[HWO_4]^-$ and/or H_2WO_4 as the pH is dependent on concentration, indicating that polymerisation has already occurred.

In contrast to the spectrophotometric results, the pH-titration results clearly show the presence of two reactions leading to the end of stage (2). An initial rapid increase in pH completed within 2 ms [corresponding to the initial curvature in the rate plots for stage (2)] is followed by a further increase completed within 500 ms. At both times the pH-titration curves (Figure 8) have comparatively sharp end-points at H : W *ca.* 1.2_5 : 1 which appear to be significantly different from the spectrophotometric end-point at H : W *ca.* 1.3_3 : 1. The pH-titration curve in the presence of 3.0 mol dm^{-3} [NMe$_4$]Cl showed a sharp end-point at H : W *ca.* 1.33 : 1 (Figure 9), also obtained by Le Meur and Souchay. (Measurements were made *ca.* 5 min after mixing, and remain unchanged over a period of *ca.* 30 min.)

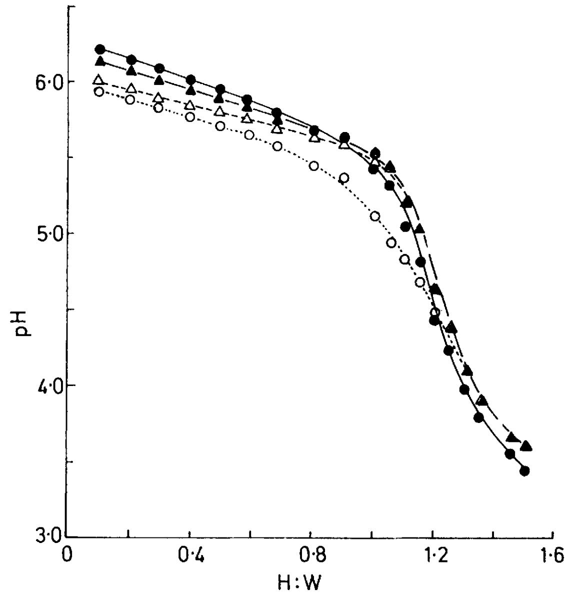

FIGURE 8 pH-Titration curves for the completion of each of the four stages at I = 0.10 mol dm^{-3} Na[ClO$_4$], 25.0 °C, and c_w = 2.00 × 10^{-3} mol dm^{-3}. Product (○) (1), (△) (2a), (▲) (2b), and (●) (3)

Stage (3) is characterised by a slow increase in pH, requiring *ca.* 1—60 s for completion, depending on H : W. The pH titration curves (Figure 8) show end-points at H : W *ca.* 1.2_0 : 1, and are clearly consistent with the expected mixture of $[HW_6O_{21}]^{5-}$ and $[(HW_6O_{20})_n]^{3n-}$.

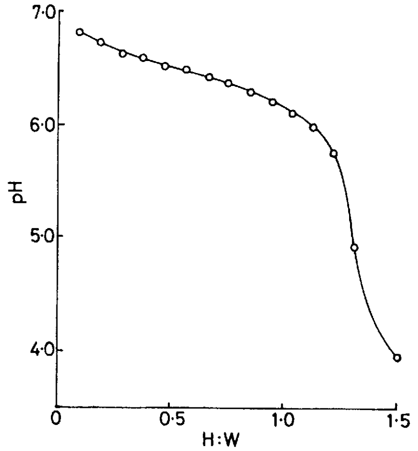

FIGURE 9 pH-Titration curve at I = 3.00 mol dm^{-3} [NMe$_4$]Cl, 25.0 °C, and c_w = 2.00 × 10^{-3} mol dm^{-3}

DISCUSSION

The spectrophotometric titrations, u.v. spectra, and pH titrations show that the product formed *ca.* 1 min after mixing acid and Na$_2$[WO$_4$] is an equilibrium mixture of $[HW_6O_{21}]^{5-}$ and $[(HW_6O_{20})_n]^{3n-}$. The spectrophotometric titrations and spectra also indicate that the major product at the end of stage (2), *ca.* 500 ms after mixing, is the 'acid paratungstate' $[H_8W_6O_{24}]^{4-}$. However, the observed curvature in the spectrophotometric-titration plots, the initial curvature in the first-order rate plots, the observation of a faster and a slower reaction in the pH results, and the apparently conflicting end-point in the pH-titration curves indicate that at least one additional minor species is also present.

Detailed calculations [10] show that the spectrophotometric- and pH-titration results for the end of stage (2) are compatible if an equilibrium mixture of two intermediate polytungstates is formed. The most satisfactory model involves six-fold condensation of both ions, the first requiring H : W = 1.17 : 1 (that is, the same as $[HW_6O_{21}]^{5-}$), and the second requiring H : W = 1.33 : 1 (that is, the same as 'acid paratungstate').

$$[H_7W_6O_{24}]^{5-} + H^+ \overset{K}{\rightleftharpoons} [H_8W_6O_{24}]^{4-} \qquad (3)$$

Using the absorption coefficient ε_8 for $[H_8W_6O_{24}]^{4-}$ obtained at H : W > 1.33 : 1 where this is the only species at the end of stage (2), it is possible to vary the absorption coefficient ε_7 for $[H_7W_6O_{24}]^{5-}$ and the equilibrium constant K to give excellent agreement with both sets of results. Excellent agreement is obtained only for $\varepsilon_7 \simeq 0$ (at 280—310 nm), and $K \simeq 4 \times 10^6$ dm^3 mol^{-1}. This value for the equilibrium constant corresponds to $[H_8W_6O_{24}]^{4-}$ always being the dominant polymer, $[H_7W_6O_{24}]^{5-}/[H_8W_6O_{24}]^{4-}$ reaching a maximum value of *ca.* 0.05 (at $c_w = 5.0 \times 10^{-4}$ mol dm^{-3}, H : W = 0.9 : 1) to 0.17 (at $c_w = 2.0 \times 10^{-3}$ mol dm^{-3}, H : W = 0.6 : 1). This agreement over the whole range of conditions is obtained only if the major species is hexameric $[H_8W_6O_{24}]^{4-}$, and only if the minor species has approximately the same degree of protonation and condensation as $[H_7W_6O_{24}]^{5-}$. For example, reasonable agreement is also obtained if the minor species is $[H_5W_4O_{16}]^{3-}$. Due to the low concentration, there is little evidence regarding the nature of the minor species beyond that it has a low absorption coefficient in the range 280—310 nm and is not observed in the spectra. It may be noted that $[HW_6O_{21}]^{5-}$ also has a low absorption coefficient in this range (Figure 3), but there is no other evidence to suggest this minor intermediate may be $[HW_6O_{21}]^{5-}$.

It should be pointed out that the two species present at the end of stage (2) may not coexist in true thermodynamic equilibrium as implied by the equilibrium constant K, but rather may coexist due to a kinetic distribution which is based on their relative rates of formation.

This treatment is obviously a simplified version of the complex equilibria and consecutive and parallel reactions which occur when acid is added to sodium tetraoxotungstate(VI) solution. The important result is that ' acid paratungstate ' $[H_8W_6O_{24}]^{4-}$, previously known only to exist in tetramethylammonium chloride solutions at high ionic strength, in which it exists for some hours, is formed as a transient intermediate in sodium perchlorate solutions and decomposes within seconds. Large cation rate effects have been noted previously in the hydrolysis of $[V_{10}O_{28}]^{6-}$,[12] $[Cr_2O_7]^{2-}$,[13] and $[Mo_7O_{24}]^{6-}$.[14]

[7/952 *Received, 2nd June,* 1977]

---

[12] B. W. Clare, D. L. Kepert, and D. W. Watts, *J.C.S. Dalton*, 1973, 2479, 2481; D. M. Druskovich and D. L. Kepert, *ibid.*, 1975, 947.

[13] B. W. Clare, D. M. Druskovich, D. L. Kepert, and J. H. Kyle, *Austral. J. Chem.*, 1977, **30**, 211.

[14] D. M. Druskovich and D. L. Kepert, *Austral. J. Chem.*, 1975, **28**, 2365.