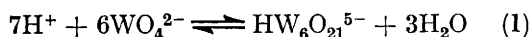


Rapid Acidification of Solutions containing Tungstate Anions

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Potentiometric titration of H^+ against tungstate, WO_4^{2-} , ions shows that the product formed in the first 0.01 s is not paratungstate A, $HW_6O_{21}^{5-}$, or any discrete ion intermediate between WO_4^{2-} and $HW_6O_{21}^{5-}$, but is a mixture of a number of ill-defined products. These may be colloidal hydrated tungsten(vi) oxides formed very rapidly in local regions of high acidity before complete mixing can occur. These are then rapidly (*ca.* 1 s) converted into $HW_6O_{21}^{5-}$. The pH was measured by an indicator-spectrophotometric technique using a stopped-flow spectrophotometer.

POLYMERISATION of tungstate ions in acidic solution has been extensively studied,¹ particularly by potentiometric techniques.² There is little doubt that the first major product is the paratungstate A anion, $HW_6O_{21}^{5-}$, formed by the addition of seven moles of acid to each six moles of tungstate ion. The structure of this hexa-



tungstate ion is unknown and no crystalline salts have been isolated, but there is again little doubt that it contains octahedrally co-ordinated tungsten atoms. The octahedra are probably not linked solely by edge sharing and it is expected that smaller units formed by edge sharing of octahedra are linked together by the sharing of octahedral corners.³

The formation of paratungstate A is complete within 1 s at room temperature. A further series of very slow reactions occurs to form more highly polymerised products^{1,4} and true equilibrium is not attained even after several months. These subsequent reactions have led to some confusion in the study of the equilibrium between the ions WO_4^{2-} and $HW_6O_{21}^{5-}$ and although a number of intermediate ions have been claimed to have been detected in significant concentrations in these partly equilibrated solutions, none could be substantiated.^{1,2} The only exception appears to be the more recently discovered $Na_2W_2O_7 \cdot 5H_2O$ obtained from very concentrated solutions during a study of the ternary system Na_2WO_4 - WO_3 - H_2O .⁵

An alternative approach for the detection of intermediate ions between WO_4^{2-} and $HW_6O_{21}^{5-}$ is to examine these solutions containing tungstate ions immediately after acidification, before complete formation of $HW_6O_{21}^{5-}$. Schwarzenbach and his co-workers⁶ potentiometrically titrated H^+ against tungstate ions in a continuous-flow apparatus (mixing time of 10^{-2} s) using very dilute solutions (*ca.* $10^{-4}M$), and found a point of inflexion at the mole ratio *ca.* 5:4 corresponding to formation of a tetratungstate ion:



The existence of other tetratungstate ions has also been mentioned but details are not yet available.^{7,8}

The object of this work was to examine the rapid

acidification of tungstate ions using stopped-flow techniques which, compared with a continuous-flow apparatus, allows the more economical use of more concentrated solutions and slightly faster mixing times, and also provides kinetic data.

EXPERIMENTAL

The pH of solutions containing tungstate ions was determined using a Durrum-Gibson stopped-flow spectrophotometer after addition of a suitable acid-base indicator.

Spectra of sulphonphthalein indicators in both the acid and base forms were not appreciably effected by the presence of tungstate ions and were used in this work. In contrast the spectra of azo-dye indicators showed considerable differences in the presence of tungstate ions suggesting the formation of complexes and were therefore not used. The pK_{In} of the sulphonphthalein indicators in the presence of tungstate ions was determined by measuring the pH of partially equilibrated solutions using a glass electrode. The pK_{In} did not depend upon the relative

Indicator	pK_{In}
Cresol Red	7.69
Bromothymol Blue	6.81
Bromocresol Purple	5.98
Bromocresol Green	4.48

amount of WO_4^{2-} and $HW_6O_{21}^{5-}$ ions or upon the age of the solution, to ± 0.01 pH units, confirming the absence of complexing between these indicators and the tungstate ions.

Reagents were of AnalaR quality and were used without further purification. Stock solutions of the indicators (B.D.H.) were prepared in water and filtered.

Solutions after mixing were 0.100M with respect to tungstate ion and 1.00M with respect to sodium nitrate, with varying amounts of nitric acid. The ratio $H^+ : WO_4^{2-}$ represents the molar ratio of H^+ to tungstate ions used.

RESULTS

The titration curve of pH against the ratio $H^+ : WO_4^{2-}$, measured immediately (0–10 ms) after mixing, is shown in the Figure. The reproducibility between different indicators is better than ± 0.1 pH units.

In the region $H^+ : WO_4^{2-} = 0$ –1.0, the pH rapidly increases with time and reaches the equilibrium value within 0.5 s. The rate of attainment of equilibrium does not

* 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 O. Glemser and W. Holtje, *Z. Naturforsch.*, 1965, b, **20**, 398; O. Glemser and K. H. Tytko, *ibid.*, 1969, b, **24**, 648; K. H. Tytko and O. Glemser, *Chimia*, 1969, **23**, 494.

⁸ A. Hullen, *Naturwiss.*, 1964, **51**, 508.

¹ D. L. Kepert, *Progr. Inorg. Chem.*, 1962, **4**, 199.

² Y. Sasaki, *Acta Chem. Scand.*, 1961, **15**, 175.

³ D. L. Kepert, *Inorg. Chem.*, 1969, **8**, 1556.

⁴ J. Aveston, *Inorg. Chem.*, 1964, **3**, 981.

⁵ E. L. Simons, *Inorg. Chem.*, 1964, **3**, 1079.

follow any obvious kinetic law, the half-life becoming progressively longer as the reaction proceeds. When the reaction was considered only over the first 2–3 half-lives, approximate first-order plots were obtained with rate

could not be obtained even for the initial pH and the rate of attainment of equilibrium also varied widely.

DISCUSSION

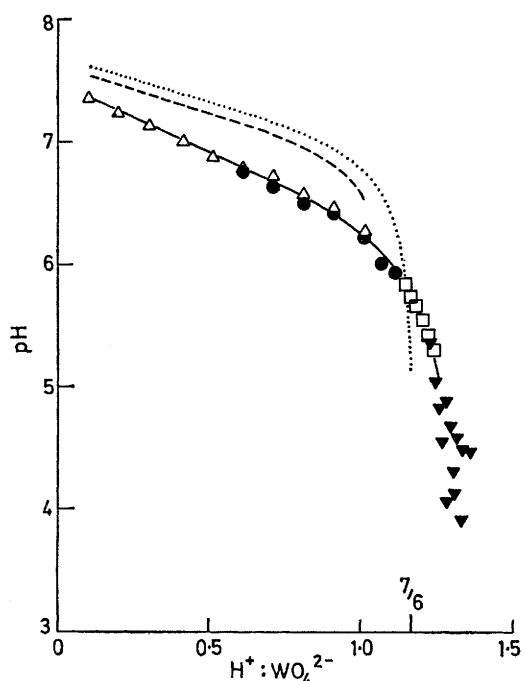
The observed titration curve is similar to that obtained by Schwarzenbach and his co-workers⁶ who interpreted the fall in pH at $H^+ : WO_4^{2-} \text{ ca. } 1.25$ as due to the tetra-tungstate ion, $H_5W_4O_{16}^{3-}$. However the more detailed results obtained here using more concentrated solutions are not consistent with a single intermediate species between the ions WO_4^{2-} and $HW_6O_{21}^{5-}$. First the slope of the straight line obtained between $H^+ : WO_4^{2-} = 0$ and 1.0 of -1.16 is much too steep for the $H_5W_4O_{16}^{3-}$ ion, the expected slope being -0.28 . This combination of steep slope and late end-point can *only* be explained by the existence of a number of species. The lack of points of inflexion between $H^+ : WO_4^{2-} = 0$ and 1.0 also shows that a number of such species must be postulated, with progressively decreasing acid dissociation constants.

Secondly the lack of reproducibility in the rate of attainment of equilibrium suggests that the products formed are dependent upon the mixing of the H^+ and tungstate ions. One plausible explanation is that these initial products are ill-defined colloidal hydrated tungsten(VI) oxides formed very rapidly in regions of high acidity before mixing is complete. These species are then more slowly converted into the $HW_6O_{21}^{5-}$ ion. The formation of species consuming more hydrogen ions than those necessary for the formation of $HW_6O_{21}^{5-}$ is also consistent with the decrease in rate of conversion of WO_4^{2-} into $HW_6O_{21}^{5-}$ as the hydrogen-ion concentration increases and the hydroxide-ion concentration decreases. Similarly the absence of a simple kinetic path is consistent with dissolution of colloidal particles.

Similar results have been obtained for the addition of H^+ to vanadate ions.⁹

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⁹ B. W. Clare, D. L. Kepert, and D. W. Watts, unpublished work.



Potentiometric titration curves for the addition of H^+ to WO_4^{2-} ions: (—), immediately (0–0.01 s) after mixing; (---), after 0.1 s; (·····), at 'infinity'. (Δ), Cresol Red; (\bullet), Bromothymol Blue; (\square), Bromocresol Purple; (\blacktriangledown), Bromocresol Green

constants decreasing from *ca.* 25 s^{-1} in the early part of the titration to *ca.* 12 s^{-1} at $H^+ : WO_4^{2-} = 1.0$. However the values obtained were not reproducible from one run to another to better than *ca.* $\pm 4 \text{ s}^{-1}$.

In the region $H^+ : WO_4^{2-} > 1.25$, reproducible values