Aust. J. Chem., 1994, **47**, 2283–2289

Nucleophilic Catalysis by HPO_4^{2-} in the Hydrolysis of $Cr_2O_7^{2-}$. Formation and Decay of $HO_3POCrO_3^{2-}$

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Abstract

The initial reaction of $Cr_2O_7^{2-}$ in phosphate buffer (pH 6·03–8·54, 25·0°C, $I = 1{\cdot}0$ M NaClO$_4$) follows the rate law $k_{\rm obs} = kK[HPO_4^{2-}]/(1+K[HPO_4^{2-}])$. This is interpreted as arising from the reversible and rapid formation of a chromium(VI)–phosphato intermediate of increased coordination number ($K = 5{\cdot}5{\pm}1{\cdot}3$ M^{-1}), and rate-determining loss of CrO_4^{2-} from this species ($k = 4{\cdot}4{\pm}0{\cdot}5$ s^{-1}) to give $HO_3POCrO_3^{2-}$ (p$K_a^c = 6{\cdot}96$). This appears to be the first clear demonstration of an addition–elimination (stepwise) mechanism for substitution at chromium (VI). Subsequent equilibration of $HO_3POCrO_3^{2-}$ to give $HCrO_4^-$ and $H_2PO_4^-$ ($K = 5{\cdot}95{\pm}\ 1{\cdot}90$ M^{-1}) is seen as a separate process which is subject to specific H$^+$ and OH$^-$, and general base (HPO_4^{2-}) catalysis, in addition to a spontaneous reaction.

Introduction

Mechanistic studies of substitution at a chromium(VI) centre have focused almost exclusively on the reaction of $HCrO_4^-$ with nucleophiles (equation *(1)*, $\mathbf{B} = H_2PO_4^-$,[1] $H_2PO_3^-$,[2] SCN$^-$,[3] $Co(NH_3)_5OH_2^{3+}$,[4] $S_2O_3^{2-}$[5]) and with oxygen-exchange processes occurring in the $Cr_2O_7^{2-}/HCrO_4^-/CrO_4^{2-}$ system.[6,7]

$$HCrO_4^- + \mathbf{B} + H^+ \rightleftharpoons \mathbf{B}CrO_3 + H_2O \qquad (1)$$

However, the recent observation of nucleophilic attack by Tris buffer on $Cr_2O_7^{2-}$ and hydrolysis of the resultant $H_3N^+C(CH_2OH)_2CH_2OCrO_3^-$ intermediate[8] has prompted us to re-examine the factors governing the reactivity of nucleophiles toward dichromate. Of the 36 oxygen and nitrogen bases used in an early study

[1] Frenesson, S. A., Beattie, J. K., and Haight, G. P., *J. Am. Chem. Soc.*, 1968, **90**, 6018.
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[3] Lin, C., and Beattie, J. K., *J. Am. Chem. Soc.*, 1972, **94**, 3011.
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[5] Muirhead, K. A., Haight, G. P., and Beattie, J. K., *J. Am. Chem. Soc.*, 1972, **94**, 3006.
[6] Okumura, A., Kitani, M., Toyami, Y., and Okazaki, N., *Bull. Chem. Soc. Jpn*, 1980, **53**, 3143.
[7] Brasch, N. E., Buckingham, D. A., and Clark, C. R., unpublished data.
[8] Brasch, N. E., Buckingham, D. A., and Clark, C. R., *Inorg. Chem.*, 1994, **33**, 2683.

Manuscript received 5 July 1994

0004-9425/94/122283$05.00

of catalysis of $Cr_2O_7{}^{2-}$ hydrolysis,[9] and another nine examined more recently,[8] only Tris has a demonstrated nucleophilic capacity, although sulfur centres in $S_2O_3{}^{2-}$[5] and glutathione[10] may also add.

We now report that the reaction of $HPO_4{}^{2-}$ with $CrO_7{}^{2-}$ in aqueous solution leads indirectly to the formation of $HO_3POCrO_3{}^{2-}$, and we describe the rate laws for the production and decay of this species. Evidence is presented which shows that the first process involves the rapid and reversible addition of $HPO_4{}^{2-}$ to $Cr_2O_7{}^{2-}$ to give a chromium(VI) intermediate of increased coordination number (five or six), and that it is the breakdown of this species to $HO_3POCrO_3{}^{2-}$ and $CrO_4{}^{2-}$ which is rate determining. A subsequent slower reaction is observed and this corresponds to equilibration of $HO_3POCrO_3{}^{2-}$ with $H_2PO_4{}^{-}$ and $HCrO_4{}^{-}$.

Experimental

Rate data were obtained by using a Durrum D-110 stopped-flow spectrophotometer coupled to a Northstar Horizon computer running OLIS software[11] for data storage and manipulation. Rate constants (k_{fast}, k_{slow}) for reactions which exhibited biphasic behaviour were obtained by use of the non-linear least-squares fitting routine V-Data Fit appropriate to a consecutive first-order reaction: $A \rightarrow B \rightarrow C$. For processes which followed pseudo-first-order kinetics, rate constants were obtained by using the linear least-squares fitting routine Normal Data Fit. Excellent fits were achieved in all cases up to 97–98% of the total absorbance change.

Reactions of $Cr_2O_7{}^{2-}$ were monitored at 470 or 442 nm following stopped-flow mixing of equal volumes of pH 4·0 chromium(VI) solution ($8\cdot33\times10^{-3}$ M, $I = 1\cdot0$ or $0\cdot02$ M ($NaClO_4$)) and $H_2PO_4{}^{-}/HPO_4{}^{2-}$ buffer ($[PO_4]_T = 0\cdot060$–$0\cdot666$ M adjusted to $I = 1\cdot0$ or $1\cdot99$ M ($NaClO_4$)). Under these conditions the reaction mixtures initially contained *c.* 43% [Cr] as $Cr_2O_7{}^{2-}$ with the remainder distributed between $HCrO_4{}^{-}$ and $CrO_4{}^{2-}$ ($K_D = [Cr_2O_7{}^{2-}]/[HCrO_4{}^{-}]^2 = 80$ M^{-1}, $pK_a^c(HCrO_4{}^{-}) = 5\cdot71$ at 25°C)[8] depending on the pH of the reaction mixture (6·03–8·54).

The reaction of monomeric chromium(VI) in phosphate buffers was followed after stopped-flow mixing of equal volumes of pH 8·5 chromium(VI) solution ($8\cdot33\times1^{-3}$ M, $I = 1\cdot0$ M) or pH or 8·0 chromium(VI) solution ($4\cdot16\times10^{-4}$ M, $I = 1\cdot0$ M) and $H_2PO_4{}^{-}/HPO_4{}^{2-}$ buffer ($I = 1\cdot0$ M), with monitoring at 450 or 350 nm respectively. Under these conditions the reaction mixtures initially contained <3% of $[Cr]_T$ as $Cr_2O_7{}^{2-}$.

Solutions of chromium(VI) were prepared from anhydrous Na_2CrO_4 (Fisher Scientific, certified) which was dried under vacuum (105°C/0·2 mmHg). Adjustment of pH was made by addition of $HClO_4$ (70% w/w). Phosphate buffers ($I = 1\cdot00$, $1\cdot99$ M) were prepared from filtered (Celite) stock solutions of NaH_2PO_4 (2·00 M), $Na_2HPO_4{}^{2-}$ (0·666 M) and $NaClO_4$ (2·00 M). pH measurements were made with a Radiometer PHM 82 pH meter equipped with G2020B (glass) and K 4040 (calomel) electrodes. Meter standardization was carried out by using phosphate (pH 6·865) and borate (pH 9·185) buffers. Acidity constants are reported as concentration constants, $K_a^c = [A^-][H^+]/[HA]$, with $[H^+] = a_{H^+}/\gamma_\pm$, $pH = -\log a_{H^+}$, $\gamma_\pm = 0\cdot767$ (25·0°C), $I = 1\cdot0$ M, $NaClO_4$.[12]

The acidity constant of $H_2PO_4{}^{-}$ at 25°C was determined by potentiometric titration of a 0·0500 M solution of Na_2HPO_4 ($I = 1\cdot0$ M, $NaClO_4$) with 1·00 M HCl, $pK_a^c = 6\cdot13\pm0\cdot04$.

Errors in rate and equilibrium constants are reported at the 99% confidence level (±3 standard deviations).

Results

The rapid decrease in absorbance observed at 470 nm following stopped-flow mixing of equal volumes of weakly acidified chromium(VI) solution (containing

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[9] Perlmutter-Hayman, B., and Wolff, M. A., *J. Phys. Chem.*, 1967, **71**, 1416; Baharad, R., Perlmutter-Hayman, B., and Wolff, M. A., *J. Phys. Chem.*, 1969, **73**, 4391.

[10] Brauer, S. L., and Wetterhahn, K. E., *J. Am. Chem. Soc.*, 1991, **113**, 3001.

[11] On-line Instrument Systems, Bogart, Georgia, U.S.A.

[12] Näsänen, R., and Meriläinen, P., *Suomen Kem.*, 1960, **3313**, 149.

43% of $[\mathrm{Cr}]_T$ as $Cr_2O_7^{2-}$) and phosphate buffer (giving $[\mathrm{Cr^{VI}}] = 4\cdot16\times10^{-3}$ M, $[\mathrm{PO_4}]_T = 0\cdot150$ M, pH 7·17) may be analysed in terms of a consecutive first-order reaction scheme $A \rightarrow B \rightarrow C$. Fig. 1 shows this with the calculated absorbance–time trace corresponding to $k_{\mathrm{fast}} = 1\cdot90\ \mathrm{s^{-1}}$, $\Delta A_{\mathrm{fast}} = -0\cdot170$, $k_{\mathrm{slow}} = 0\cdot150\ \mathrm{s^{-1}}$, $\Delta A_{\mathrm{slow}} = -0\cdot150$, which give excellent agreement with the observed data. It was not possible to find a wavelength where the absorbance changes were in opposite senses, and in the range 445–500 nm both processes gave rise to absorbance decreases. However, the difference in the two reaction rates ($k_{\mathrm{fast}}/k_{\mathrm{slow}} = 13$) was such as to remove ambiguity from the analysis* and it allowed both rate constants to be well defined. The first observed reaction is consequently equated with the first mechanistic process. Also, studies at 442 nm showed that this wavelength is an isosbestic for the second process, and absorbance–time data at 442 nm analysed as a single exponential corresponding to k_{fast} irrespective of the reaction conditions (pH 6·03–7·21, $[\mathrm{PO_4}]_T = 0\cdot05$–$0\cdot400$ M). Rate constants k_{fast} and k_{slow} found from studies at 470 and 442 nm, and over the pH range 6·03–8·54 at $[\mathrm{PO_4}]_T = 0\cdot030$–$0\cdot400$ M, are given in Table 1.

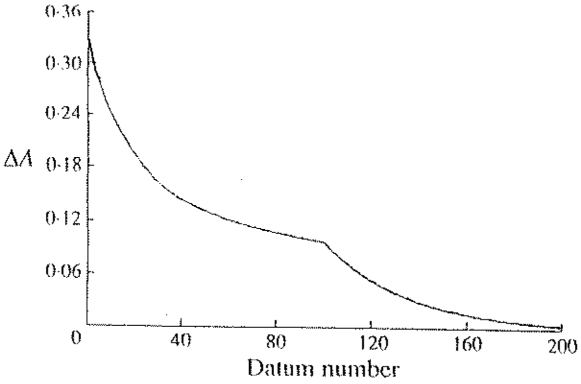

Fig. 1. Calculated and observed changes in absorbances with time at 470 nm for hydrolysis of $Cr_2O_7^{2-}$ in the presence of phosphate buffer, $[\mathrm{PO_4}]_T = 0\cdot150$ M, $[\mathrm{Cr}]_T = 4\cdot16\times10^{-3}$ M, pH 7·17. The time axis is split, with the first 100 datum points collected over 3 s and the remaining 100 collected over 20 s. The 'infinity' absorbance was recorded after 38 s reaction. The fit superimposed on the observed data uses $k_{\mathrm{fast}} = 1\cdot90\ \mathrm{s^{-1}}$, $\Delta A_{\mathrm{fast}} = -0\cdot170$, $k_{\mathrm{slow}} = 0\cdot150\ \mathrm{s^{-1}}$, $\Delta A_{\mathrm{slow}} = -0\cdot150$.

When the chromium(VI) reagent used in the stopped-flow experiments contained only $HCrO_4^-$ and CrO_4^{2-} (i.e. no significant $Cr_2O_7^{2-}$), the reaction with phosphate buffer gave rise to a single first-order process. Table 2 gives rate constants obtained at 350 nm corresponding to reaction at $[\mathrm{Cr}]_T = 2\cdot08\times10^4$ M, and at 450 nm corresponding to reaction at $[\mathrm{Cr}]_T = 4\cdot16\times10^{-3}$ M.

No attempt was made to analyse the absorbance changes associated with the reactions since, in general, both the initial and final absorbances were dependent on the solution pH as a consequence of the changing distribution of monomeric and dimeric chromium(VI) species (see below). This factor also limited the pH range used. For example, the absorbance change at 350 nm was too small ($<0\cdot02$ for $[\mathrm{Cr}]_T = 2\cdot08\times10^{-4}$ M) to be useful in the reaction of monomeric chromium(VI) at pH $> 6\cdot4$. Similarly, at pH $< 6\cdot3$ diminishing absorbances associated with the second process in the biphasic reaction prevented analysis of kinetic data collected under these acidity conditions.

Discussion

The first observed reaction of $Cr_2O_7^{2-}$ with phosphate is interpreted as arising from nucleophilic attack by HPO_4^{2-} with rapid and reversible formation of a five-

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* For a discussion of contributing factors, see ref. 13.

[13] Jackson, W. G., Harrowfield, J. M., and Vowles, P. D., *Int. J. Chem. Kin.*, 1977, **9**, 535.

Table 1. Observed and calculated first-order rate constants (k_{fast}, k_{slow}) for the reaction of $Cr_2O_7^{2-}$ in phosphate buffers, 25°C, $I = 1\cdot0$ M ($NaClO_4$)

Rate constants measured at 470 nm unless otherwise stated; $[Cr]_T = 4\cdot16\times10^{-3}$ M

pH	$10^7[H^+]$/ M	$[PO_4]_T$/ M	k_{fast}/s^{-1} Obs.	k_{fast}/s^{-1} Calc.[A]	k_{slow}/s^{-1} Obs.	k_{slow}/s^{-1} Calc.[B]
6·03	12·16	0·300	1·71[C]	1·71		
6·16	9·02	0·250	1·69[C]	1·70		
6·23	7·68	0·050	0·583[C]	0·540		
6·31	6·39	0·100	1·01[C]	1·03		
6·33	6·10	0·100	1·00	1·04	0·198	0·217
6·35	5·83	0·150	1·53	1·41	0·270	0·243
6·38	5·44	0·200	1·72[C]	1·73		
6·39	5·31	0·200	1·80	1·74	0·267	0·268
6·42	4·95	0·200	1·80	1·77	0·285	0·265
6·48	4·32	0·400	2·47[C]	2·55		
6·58	3·43	0·0433	0·650	0·634	0·150	0·165
6·69	2·66	0·0867	1·01	1·16	0·175	0·177
6·71	2·54	0·300	2·40	2·42	0·270	0·281
6·76	2·27	0·130	1·52	1·57	0·196	0·190
6·82	1·97	0·174	1·95	1·90	0·200	0·202
6·89	1·68	0·200	2·20	2·09	0·207	0·204
6·90	1·64	0·100	1·35[C]	1·39		
6·90	1·64	0·100	1·34	1·39	0·158	0·159
7·12	0·990	0·0300	0·488	0·575	0·095	0·107
7·17	0·881	0·150	1·90	1·88	0·150	0·142
7·17	0·881	0·150	1·89[C]	1·88		
7·18	0·862	0·100	1·50	1·47	0·128	0·124
7·21	0·804	0·100	1·40[C]	1·48		
7·36	0·570	0·220	2·27	2·32	0·137	0·134
7·54	0·376	0·270	2·53	2·56	0·120	0·116
7·66	0·286	0·310	2·67	2·71	0·117	0·105
8·04	0·119	0·167	2·07	2·09	0·0467	0·0503
8·54	0·375	0·333	2·80	2·81	0·0370	0·0360

[A] Calculated values of k_{fast} according to equation *(2)* and the values of the constants given in the text.

[B] Calculated values of k_{slow} according to equation *(3)* and the values of the constants given in the text.

[C] Measured at 442 nm.

or six-coordinate chromium(VI)–phosphato intermediate (K) which subsequently undergoes rate-determining loss of CrO_4^{2-} (k) to give HO_3POCrO_3, Scheme 1. This mechanism is suggested by the curvature in the plot of k_{fast} v. $[HPO_4^{2-}]$, Fig. 2, with k_{fast} approaching a limiting value at high $[HPO_4^{2-}]$. Accordingly the variation of k_{fast} with $[HPO_4^{2-}]$ is given by equation *(2)* with $K = 5\cdot5\pm1\cdot3$ M^{-1} and $k = 4\cdot4\pm0\cdot5$ s^{-1} (HPO_4^{2-} concentrations were calculated from $[PO_4]_T$ and pH by using a measured value of the acidity constant for $H_2PO_4^-$, $K^c_{a1} = (7\cdot5\pm0\cdot8)\times10^{-7}$ M at $I = 1\cdot0$ M ($NaClO_4$), 25°C). Values of k_{fast} calculated according to equation *(2)* are included in Table 1 and show good agreement with the observed values.

$$k_{\mathrm{fast}} = \frac{kK[HPO_4^{2-}]}{1 + K[HPO_4^{2-}]} \qquad (2)$$

Table 2. Observed and calculated first-order rate constants for the reaction of monomeric chromium(VI) in phosphate buffer, 25·0°C, $I = 1\cdot0$ M ($NaClO_4$)

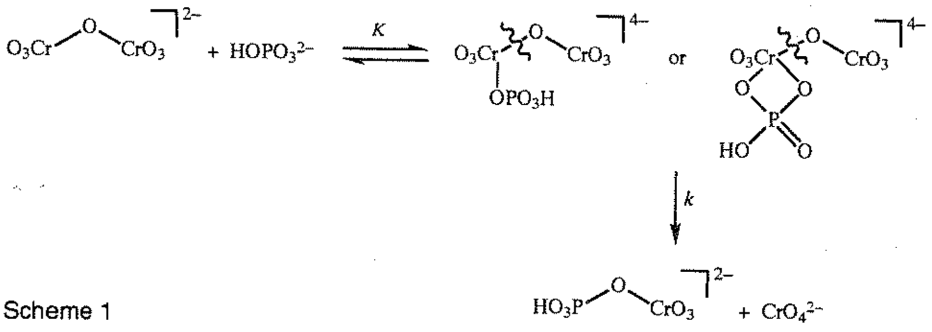
Rate constants obtained following mixing of chromium(VI) solution, initially at pH 8.0, with phosphate buffer and observation at 350 nm unless otherwise stated. $[Cr]_T = 2\cdot08\times10^{-4}$ M

pH	$10^6[H^+]$/M	$[PO_4]_T$/M	k_{obs}/s^{-1}	k_{calc}/s^{-1} [A]
5·02	12·5	0·213	0·849, 0·863[B]	0·868
5·03	12·2	0·160	0·735, 0·719[B]	0·742
5·04	11·9	0·1067	0·607, 0·597[B]	0·621
5·07	11·1	0·0533	0·494, 0·485[B]	0·491
5·33	6·10	0·2333	0·619	0·607
5·33	6·10	0·170	0·533	0·491
5·33	6·10	0·1133	0·441	0·439
5·34	5·96	0·0567	0·389	0·360
6·39	5·31	0·0500	0·186[C]	0·185
6·41	5·07	0·100	0·219[C]	0·210
6·42	4·95	0·200	0·278	0·265
6·43	4·85	0·150	0·233[C]	0·235
6·45	4·63	0·200	0·268[C]	0·262

[A] Rate constants calculated according to equation *(3)* and the values of constants given in the text.

[B] Chromium(VI) solution initially pH 4·5.

[C] Chromium(VI) solution initially pH 8·5, $[Cr]_T = 4\cdot16\times10^{-3}$ M, 450 nm.



Scheme 1

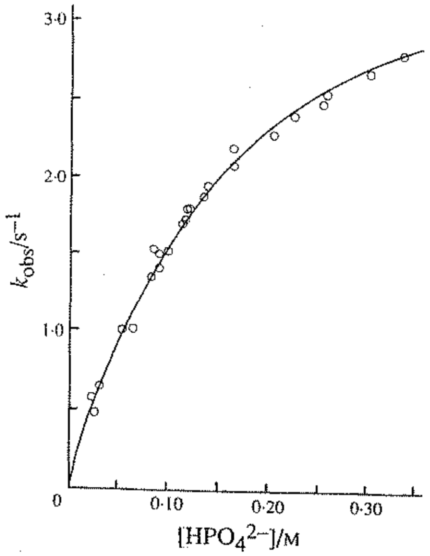
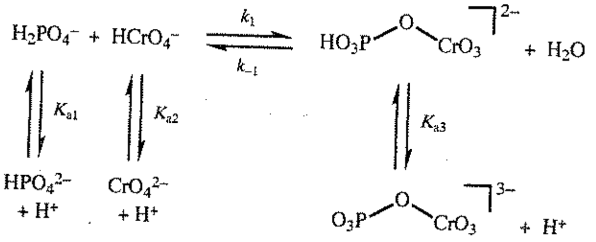


Fig. 2. Variation of k_{fast} ($= k_{obs}$) with $[HPO_4^{2-}]$ for reaction of $Cr_2O_7^{2-}$ in phosphate buffer at 25°C and $I = 1\cdot0$ M ($NaClO_4$). The points are experimental data and the curve is drawn with use of equation *(2)* and the values of the constants given in the text.

We favour this mechanism over one involving ion pair formation between $Cr_2O_7^{2-}$ and HPO_4^{2-} with product formation arising from a pre-associated $HPO_4^{2-}.Cr_2O_7^{2-}$ species. This would require $K_{IP}(=K) = 5 \cdot 5\ \text{M}^{-1}$, a value more in keeping with a (2+).(1−) ion pair* than one involving two 2− charged ions.

Coordination numbers greater than four are known in chromium(VI)–oxo chemistry. Thus, six-coordinate η^2,η^2-$[CrO(O_2)_2(py)]$ is produced on treating $Cr_2O_7^{2-}(aq)$ with H_2O_2 and workup from ethereal pyridine,[16] and the related η^2,η^2-$[CrO(O_2)_2(bpy)]$ has been shown to be seven-coordinate.[17] Also, the direct pathways for oxygen exchange into $Cr_2O_7^{2-}(aq)$[7] and $HCrO_4^-(aq)$[6,7] might suggest the presence of five-coordinate hydrated intermediates. In the present study the kinetic data appear to require the intermediacy of a chromium(VI) species of increased coordination number, and that its breakdown to products is rate determining.



Scheme 2

The second observed reaction corresponds to relaxation according to Scheme 2. For this process the observed first-order rate constant, k_{slow}, follows equation *(3)*, with K^c_{a2} corresponding to the known acidity constant of $HCrO_4^-$ at 25°C and $I = 1 \cdot 0$ M ($1 \cdot 97 \times 10^{-6}$ M), and K^c_{a3} to the acidity constant of $HO_3POCrO_3^{2-}$.

$$k_{\text{slow}} = \frac{k_1[PO_4]_T[H^+]^2}{(K^c_{a1} + [H^+])(K^c_{a2} + [H^+])} + \frac{k_{-1}[H^+]}{(K^c_{a3} + [H^+])} \qquad (3)$$

Least-squares fitting of the data (Table 1) was carried out with the recognition that pathways established for the hydrolysis of $Cr_2O_7^{2-}$[8,9] were also likely for the hydrolysis of $HO_3POCrO_3^{2-}$. Accordingly, contributions to k_{-1} (and concomitantly to k_1) are found for the spontaneous reaction, from acid catalysis, from general base (HPO_4^{2-}) and from specific OH^- catalysis. Thus:

$$k_{-1} = k_o + k_H[H^+] + k_{HPO_4}[HPO_4^{2-}] + k_{OH}[OH^-] \qquad (4)$$

and a good fit to equation *(3)* is achieved by using $k_o = 0 \cdot 177 \pm 0 \cdot 055\ \text{s}^{-1}$, $k_H = (1 \cdot 94 \pm 0 \cdot 40) \times 10^4\ \text{M}^{-1}\ \text{s}^{-1}$, $k_{HPO_4} = 0 \cdot 8717 \pm 0 \cdot 413\ \text{M}^{-1}\ \text{s}^{-1}$, $k_{OH} = (2 \cdot 4 \pm 1 \cdot 2) \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$, a value for K_{a3} of $(1 \cdot 09 \pm 0 \cdot 65) \times 10^{-7}$ M and a k_1/k_{-1}

* The Fuoss equation[14] predicts values of 1–5 M^{-1} for this combination.[15]

[14] Fuoss, R. M., *J. Am. Chem. Soc.*, 1958, **80**, 5059.

[15] Boreham, C. J., Buckingham, D. A., and Clark, C. R., *Inorg. Chem.*, 1979, **18**, 1990.

[16] Pedersen, B. F., and Pedersen, B., *Acta Chem. Scand.*, 1963, **17**, 557.

[17] Stomberg, R., and Ainalem, I.-B., *Acta Chem. Scand.*, 1968, **22**, 1439.

ratio of $5{\cdot}95\pm1{\cdot}90\ \mathrm{M}^{-1}$. The k_1/k_1 ratio defines the formation constant of $HO_3POCrO_3^{2-}$.* This has previously been directly determined at 25°C as having values of $2{\cdot}9\pm0{\cdot}8\ \mathrm{M}$ at $I = 0{\cdot}25\ \mathrm{M}$ [18] and $6\pm2\ \mathrm{M}^{-1}$ at $I = 3{\cdot}0\ \mathrm{M}^{-1}$.[1] The $\mathrm{p}K^{\mathrm{c}}_{\mathrm{a3}}$ value of $6{\cdot}96\pm0{\cdot}40$ shows that $HO_3POCrO_3^{2-}$ is a slightly weaker acid than $H_2PO_4^-$ ($\mathrm{p}K^{\mathrm{c}}_{\mathrm{a1}} = 6{\cdot}13\pm0{\cdot}04$).

The above interpretation was verified through a direct study of the kinetics of formation of $HO_3POCrO_3^{2-}$ from monomeric $HCrO_4^-$. Good agreement is seen (Table 2) between the observed rate constants and those calculated from equation *(3)* and the above values for the rate and equilibrium parameters. This latter study also supplements that of Haight *et al.*[1] who established Cr–O bond cleavage and H^+ and general acid–base catalysis in the hydrolysis of $HO_3POCrO_3^{2-}$ ($\mathrm{pH} \leq 5$, $I = 3{\cdot}0\ \mathrm{M}$).†

Some comment on the factors which govern the reactivity of oxy anions as nucleophiles toward $Cr_2O_7^{2-}$, and which favour the observation of $\mathbf{B}CrO_3$ intermediates, is appropriate. Firstly, although both Tris and HPO_4^{2-} are able to function as chelating agents, the ability to chelate is not a requirement. Thus in the presence of several potential N–O chelates,[8] and in HCO_3^-/CO_3^{2-} and $HC_2O_4^-/C_2O_4^{2-}$ media,[7] $Cr_2O_7^{2-}$ is hydrolysed smoothly to CrO_4^{2-} without the accumulation of a detectable intermediate (pseudo-first-order kinetics). This does not preclude a nucleophilic pathway, but it does mean that any addition product must be hydrolysed much more rapidly than it is formed. This is certainly a possibility since the H^+- and OH^--catalysed pathways shown here for HO_3POCrO_3 may allow only a narrow pH window for the detection of such an intermediate, especially when its stability is substantially less than that of $Cr_2O_7^{2-}$ itself. Secondly, since the hydrolysis of $\mathbf{B}CrO_3$ species ($\mathbf{B}$ = Tris,[8] HO_3PO,[1] O_2HPO [2]) is known to be subject to general base catalysis (see above) this must also be true of $Cr_2O_7^{2-}$ ($\mathbf{B} = O_3CrO$) so that a direct pathway to hydrolysed products is always present. Any contribution made by the indirect nucleophilic pathway is presumably determined by the steric, electronic and, possibly, lack of hydrogen-bonding properties of $\mathbf{B}$.

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* This species gives rise to a ^{31}P n.m.r. signal at $3{\cdot}20$ ppm (relative to H_3PO_4 external reference) in aqueous solutions containing $16{\cdot}7\%$ D_2O, $I = 1{\cdot}0\ \mathrm{M}$, 25°C.

† Where comparison is possible good agreement is seen between rate constants determined in the two studies, e.g. $k_{\mathrm{H}} = 1{\cdot}9\times10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in the present work compared to $k_{\mathrm{H}} = 2{\cdot}0\times10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ reported in ref. 1. Many of the processes, however, can be interpreted in terms of kinetically indistinguishable alternative mechanisms. See, for example, ref. 19.

[18] Holloway, F., *J. Am. Chem. Soc.*, 1952, **74**, 224.

[19] Haim, A., *Inorg. Chem.*, 1972, **11**, 3147.