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

Nicola E. Brasch,^A David A. Buckingham^{A,B} and Charles R. Clark^A

^A Department of Chemistry, University of Otago,

P.O. Box 56, Dunedin, New Zealand.

^B Author to whom correspondence should be addressed.

Abstract

The initial reaction of $\text{Cr}_2\text{O7}^{2-}$ in phosphate buffer (pH $6\cdot03-8\cdot54$, $25\cdot0^\circ\text{C}$, $I = 1\cdot0$ M NaClO₄) follows the rate law $k_{\text{obs}} = kK[\text{HPO4}^{2-}]/(1+K[\text{HPO4}^{2-}])$. This is interpreted as arising from the reversible and rapid formation of a chromium(vI)-phosphato intermediate of increased coordination number ($K = 5\cdot5\pm1\cdot3$ M⁻¹), and rate-determining loss of CrO4^{2-} from this species ($k = 4\cdot4\pm0\cdot5$ s⁻¹) to give HO₃POCrO3²⁻ (pK_a^c = 6\cdot96). This appears to be the first clear demonstration of an addition-elimination (stepwise) mechanism for substitution at chromium (vI). Subsequent equilibration of HO₃POCrO3²⁻ to give HCrO4⁻ and H₂PO4⁻ ($K = 5\cdot95\pm1\cdot90$ M⁻¹) is seen as a separate process which is subject to specific H⁺ and OH⁻, and general base (HPO4²⁻) 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}

$$HCrO_4^- + \mathbf{B} + H^+ \rightleftharpoons \mathbf{B}CrO_3 + H_2O \tag{1}$$

However, the recent observation of nucleophilic attack by Tris buffer on $Cr_2O_7^{2-}$ and hydrolysis of the resultant $H_3N^+C(CH_2OH)_2CH_2OCrO_3^-$ intermediate⁸ 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

² Frenesson, S. A., Beattie, J. K., and Haight, G. P., Acta Chem. Scand., 1969, 23, 3277.

³ Lin, C., and Beattie, J. K., J. Am. Chem. Soc., 1972, 94, 3011.

⁵ Muirhead, K. A., Haight, G. P., and Beattie, J. K., J. Am. Chem. Soc., 1972, 94, 3006.

Manuscript received 5 July 1994

0004-9425/94/122283\$05.00

¹ Frenesson, S. A., Beattie, J. K., and Haight, G. P., J. Am. Chem. Soc., 1968, 90, 6018.

⁴ Grace, M. R., and Tregloan, P. A., *Inorg. Chem.*, 1992, **31**, 4524; Sadler, N. P., and Dasgupta, T. P., *Transition Met. Chem.*, 1992, **17**, 317.

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.

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 glutathione¹⁰ 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 $\text{HO}_3\text{POCrO}_3^{2-}$, 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 $\text{Cr}_2\text{O}_7^{2-}$ to give a chromium(VI) intermediate of increased coordination number (five or six), and that it is the breakdown of this species to $\text{HO}_3\text{POCrO}_3^{2-}$ and CrO_4^{2-} which is rate determining. A subsequent slower reaction is observed and this corresponds to equilibration of $\text{HO}_3\text{POCrO}_3^{2-}$ with $\text{H}_2\text{PO}_4^{-}$ 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 software¹¹ 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 $\operatorname{Cr}_2\operatorname{O_7}^{2-}$ were monitored at 470 or 442 nm following stopped-flow mixing of equal volumes of pH 4.0 chromium(VI) solution $(8\cdot33\times10^{-3} \text{ M}, I = 1\cdot0 \text{ or } 0\cdot02 \text{ M})$ (NaClO₄)) and H₂PO₄⁻/HPO₄²⁻ buffer ([PO₄]_T = $0\cdot060-0\cdot666 \text{ M}$ adjusted to $I = 1\cdot0$ or $1\cdot99 \text{ M}$ (NaClO₄)). Under these conditions the reaction mixtures initially contained c. 43% [Cr] as $\operatorname{Cr}_2\operatorname{O_7}^{2-}$ with the remainder distributed between HCrO₄⁻ and CrO₄²⁻ ($K_D = [\operatorname{Cr}_2\operatorname{O_7}^{2-}]/[\operatorname{HCrO_4}^{-}]^2 = 80 \text{ M}^{-1}$, $pK_a^c(\operatorname{HCrO_4}^{-}) = 5\cdot71$ at 25° C)⁸ depending on the pH of the reaction mixture ($6\cdot03-8\cdot54$).

The reaction of monomeric chromium(VI) in phosphate buffers was followed after stoppedflow mixing of equal volumes of pH 8.5 chromium(VI) solution $(8.33 \times 1^{-3} \text{ M}, I = 1.0 \text{ M})$ or pH or 8.0 chromium(VI) solution $(4.16 \times 10^{-4} \text{ M}, I = 1.0 \text{ M})$ and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer (I = 1.0 M), with monitoring at 450 or 350 nm respectively. Under these conditions the reaction mixtures initially contained <3% of $[\text{Cr}]_T$ as $\text{Cr}_2\text{O}_7^{2-}$.

Solutions of chromium(VI) were prepared from anhydrous Na₂CrO₄ (Fisher Scientific, certified) which was dried under vacuum (105°C/0·2 mmHg). Adjustment of pH was made by addition of HClO₄ (70% w/w). Phosphate buffers (I = 1.00, 1.99 M) were prepared from filtered (Celite) stock solutions of NaH₂PO₄ (2·00 M), Na₂HPO₄²⁻ (0.666 M) and NaClO₄ (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 = $-\log a_{H^+}$, $\gamma_{\pm} = 0.767$ (25·0°C), I = 1.0 M, NaClO₄.¹²

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 = 1.0 M, $NaClO_4$) with 1.00 M HCl, $pK_a^c = 6.13\pm0.04$.

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

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 $[Cr]_T$ as $Cr_2O_7^{2-}$) and phosphate buffer (giving $[Cr^{VI}] = 4 \cdot 16 \times 10^{-3}$ M. $[PO_4]_T = 0.150 \text{ M}$, 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 absorbancetime trace corresponding to $k_{\text{fast}} = 1.90 \text{ s}^{-1}$, $\Delta A_{\text{fast}} = -0.170$, $k_{\text{slow}} = 0.150 \text{ s}^{-1}$, $\Delta A_{\rm slow} = -0.150$, 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 $(k_{\text{fast}}/k_{\text{slow}} = 13)$ 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, $[PO_4]_T = 0.05-0.400$ M). Rate constants k_{fast} and k_{slow} found from studies at 470 and 442 nm, and over the pH range $6 \cdot 03 - 8 \cdot 54$ at $[PO_4]_T = 0 \cdot 030 - 0 \cdot 400$ M, are given in Table 1.



Fig. 1. Calculated and observed changes in absorbances with time at 470 nm for hydrolysis of $\text{Cr}_2\text{O7}^{2-}$ in the presence of phosphate buffer, $[\text{PO}_4]_{\rm T} = 0.150$ M, $[\text{Cr}]_{\rm T} = 4.16 \times 10^{-3}$ 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 $k_{\rm fast} = 1.90 \text{ s}^{-1}$, $\Delta A_{\rm fast} = -0.170$, $k_{\rm slow} = 0.150 \text{ s}^{-1}$, $\Delta A_{\rm slow} = -0.150$.

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 $[Cr]_T = 2.08 \times 10^4$ M, and at 450 nm corresponding to reaction at $[Cr]_T = 4.16 \times 10^{-3}$ 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 (<0.02 for $[Cr]_T = 2.08 \times 10^{-4}$ M) to be useful in the reaction of monomeric chromium(VI) at pH > 6.4. Similarly, at pH < 6.3 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-

* 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.

pН	$10^{7}[H^{+}]/$	$[PO_4]_T/$	$k_{\rm fast}/{\rm s}^{-1}$		$k_{\rm slow}/{\rm s}^{-1}$	
	М	М	Obs.	Calc. ^A	Obs.	Calc. ^B
6.03	$12 \cdot 16$	0.300	1.71 ^C	1.71		
$6 \cdot 16$	9.02	0.250	$1 \cdot 69^{\mathbf{C}}$	1.70		
$6 \cdot 23$	7.68	0.050	$0.583^{ m C}$	0.540		
6.31	6.39	0.100	$1 \cdot 01^{\mathbf{C}}$	$1 \cdot 03$		
6.33	6.10	0.100	$1 \cdot 00$	1.04	0.198	0.217
6.35	5.83	0.150	1.53	$1 \cdot 41$	0.270	0.243
6.38	5.44	0.200	$1 \cdot 72^{\mathbf{C}}$	1.73		
6.39	5.31	0.200	$1 \cdot 80$	1.74	0.267	0.268
$6 \cdot 42$	4.95	$0 \cdot 200$	1.80	1.77	0.285	0.265
6.48	$4 \cdot 32$	0.400	$2 \cdot 47^{\mathbf{C}}$	2.55		
6.58	$3 \cdot 43$	0.0433	0.650	0.634	0.150	0.165
$6 \cdot 69$	2.66	0.0867	$1 \cdot 01$	$1 \cdot 16$	0.175	0.177
6.71	$2 \cdot 54$	0.300	$2 \cdot 40$	$2 \cdot 42$	0.270	0.281
6.76	$2 \cdot 27$	0.130	$1 \cdot 52$	1.57	0.196	0.190
6.82	1.97	0.174	$1 \cdot 95$	$1 \cdot 90$	$0 \cdot 200$	$0 \cdot 202$
$6 \cdot 89$	1.68	$0 \cdot 200$	$2 \cdot 20$	$2 \cdot 09$	0.207	0.204
6.90	1.64	0.100	$1 \cdot 35^{\rm C}$	1.39		
6.90	$1 \cdot 64$	0.100	$1 \cdot 34$	$1 \cdot 39$	0.158	0.159
$7 \cdot 12$	0.990	0.0300	0.488	0.575	0.095	0.107
7.17	0.881	0.150	$1 \cdot 90$	1.88	0.150	$0 \cdot 142$
$7 \cdot 17$	0.881	0.150	$1 \cdot 89^{C}$	1.88		
$7 \cdot 18$	0.862	0.100	$1 \cdot 50$	$1 \cdot 47$	0.128	$0 \cdot 124$
$7 \cdot 21$	0.804	0.100	$1 \cdot 40^{C}$	$1 \cdot 48$		
7.36	0.570	0.220	$2 \cdot 27$	$2 \cdot 32$	0.137	0.134
7.54	0.376	0.270	$2 \cdot 53$	$2 \cdot 56$	0.120	0.116
7.66	0.286	0.310	$2 \cdot 67$	$2 \cdot 71$	0.117	0.105
8.04	0.119	0.167	$2 \cdot 07$	$2 \cdot 09$	0.0467	0.0503
8.54	0.375	0.333	$2 \cdot 80$	$2 \cdot 81$	0.0370	0.0360
7 · 36 7 · 54 7 · 66 8 · 04 8 · 54	$0.570 \\ 0.376 \\ 0.286 \\ 0.119 \\ 0.375$	$0.220 \\ 0.270 \\ 0.310 \\ 0.167 \\ 0.333$	$2 \cdot 27$ $2 \cdot 53$ $2 \cdot 67$ $2 \cdot 07$ $2 \cdot 80$	$2 \cdot 32$ $2 \cdot 56$ $2 \cdot 71$ $2 \cdot 09$ $2 \cdot 81$	$0.137 \\ 0.120 \\ 0.117 \\ 0.0467 \\ 0.0370$	

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 = 1.0 M (NaClO₄)

^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.

 $^{\rm C}$ 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 HO₃POCrO₃, Scheme 1. This mechanism is suggested by the curvature in the plot of $k_{\text{fast}} v$. [HPO₄²⁻], Fig. 2, with k_{fast} approaching a limiting value at high [HPO₄²⁻]. Accordingly the variation of k_{fast} with [HPO₄²⁻] is given by equation (2) with $K = 5 \cdot 5 \pm 1 \cdot 3 \text{ M}^{-1}$ and $k = 4 \cdot 4 \pm 0 \cdot 5 \text{ s}^{-1}$ (HPO₄²⁻ concentrations were calculated from [PO₄]_T and pH by using a measured value of the acidity constant for H₂PO₄⁻, $K_{a1}^c = (7 \cdot 5 \pm 0 \cdot 8) \times 10^{-7} \text{ M at } I = 1 \cdot 0 \text{ M} (\text{NaClO}_4), 25^{\circ}\text{C})$. Values of k_{fast} calculated according to equation (2) are included in Table 1 and show good agreement with the observed values.

$$k_{\text{fast}} = \frac{kK[\text{HPO}_4^{2-}]}{1 + K[\text{HPO}_4^{2-}]}$$
(2)

Table 2. Observed and calculated first-order rate constants for the reaction of monomeric chromium(VI) in phosphate buffer, 25.0° C, I = 1.0 M (NaClO₄)

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. $[Cr]_T = 2.08 \times 10^{-4}$ M

pН	10 ⁶ [H ⁺]/м	[PO ₄] _Т /м	$k_{ m obs}/{ m s}^{-1}$	$k_{\rm calc}/{\rm s}^{-1}{}^{\rm A}$
$5 \cdot 02$	12.5	0.213	$0.849, 0.863^{B}$	0.868
5.03	$12 \cdot 2$	0.160	$0.735, 0.719^{B}$	0.742
5.04	$11 \cdot 9$	0.1067	$0.607, 0.597^{B}$	0.621
5.07	$11 \cdot 1$	0.0533	$0.494, 0.485^{B}$	0.491
5.33	$6 \cdot 10$	0.2333	0.619	0.607
5.33	$6 \cdot 10$	0.170	0.533	0.491
5.33	$6 \cdot 10$	0.1133	0.441	0.439
5.34	5.96	0.0567	0.389	0.360
6.39	$5 \cdot 31$	0.0500	0.186^{C}	0.185
$6 \cdot 41$	$5 \cdot 07$	0.100	$0\cdot 219^{\mathbf{C}}$	$0 \cdot 210$
$6 \cdot 42$	$4 \cdot 95$	0.200	0.278	0.265
$6 \cdot 43$	$4 \cdot 85$	0.150	$0.233^{ m C}$	0.235
$6 \cdot 45$	$4 \cdot 63$	0.200	$0 \cdot 268^{\mathbf{C}}$	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, $[Cr]_T = 4.16 \times 10^{-3}$ M, 450 nm.



Fig. 2. Variation of k_{fast} (= k_{obs}) with [HPO₄²⁻] for reaction of $\text{Cr}_2\text{O}_7^{2-}$ in phosphate buffer at 25°C and I = 1.0 M (NaClO₄). 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.



0.30

[HPO42-]/M

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 $K_{\rm IP}(=K) = 5 \cdot 5 \,{\rm M}^{-1}$, 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(O₂)₂(py)] is produced on treating Cr₂O₇²⁻(aq) with H₂O₂ and workup from ethereal pyridine,¹⁶ and the related η^2 , η^2 -[CrO(O₂)₂(bpy)] has been shown to be seven-coordinate.¹⁷ Also, the direct pathways for oxygen exchange into Cr₂O₇²⁻(aq)⁷ and HCrO₄⁻(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.



The second observed reaction corresponds to relaxation according to Scheme 2. For this process the observed first-order rate constant, $k_{\rm slow}$, follows equation (3), with $K_{\rm a2}^{\rm c}$ corresponding to the known acidity constant of $\rm HCrO_4^-$ at 25°C and $I = 1.0 \,\mathrm{M} \, (1.97 \times 10^{-6} \,\mathrm{M})$, and $K_{\rm a3}^{\rm c}$ to the acidity constant of $\rm HO_3 POCrO_3^{2-}$.

$$k_{\rm slow} = \frac{k_1 [\rm PO_4]_T [\rm H^+]^2}{(K_{a1}^c + [\rm H^+])(K_{a2}^c + [\rm H^+])} + \frac{k_{-1} [\rm H^+]}{(K_{a3}^c + [\rm H^+])}$$
(3)

Least-squares fitting of the data (Table 1) was carried out with the recognition that pathways established for the hydrolysis of $\text{Cr}_2\text{O}_7^{2-8,9}$ were also likely for the hydrolysis of $\text{HO}_3\text{POCrO}_3^{2-}$. 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:

$$k_{-1} = k_{\rm o} + k_{\rm H}[{\rm H}^+] + k_{\rm HPO_4}[{\rm HPO_4}^{2-}] + k_{\rm OH}[{\rm OH}^-]$$
(4)

and a good fit to equation (3) is achieved by using $k_{\circ} = 0.177 \pm 0.055 \text{ s}^{-1}$, $k_{\text{H}} = (1.94 \pm 0.40) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{HPO}_4} = 0.8717 \pm 0.413 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{OH}} = (2.4 \pm 1.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, a value for K_{a3} of $(1.09 \pm 0.65) \times 10^{-7} \text{ M}$ and a k_1/k_{-1}

- 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.

^{*} The Fuoss equation¹⁴ predicts values of $1-5 \text{ M}^{-1}$ 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.

ratio of $5.95\pm1.90 \text{ M}^{-1}$. The k_1/k_1 ratio defines the formation constant of $\text{HO}_3\text{POCrO}_3^{2-}$.* This has previously been directly determined at 25°C as having values of $2.9\pm0.8 \text{ M}$ at $I = 0.25 \text{ M}^{18}$ and $6\pm2 \text{ M}^{-1}$ at $I = 3.0 \text{ M}^{-1}$.¹ The p K_{a3}^c value of 6.96 ± 0.40 shows that $\text{HO}_3\text{POCrO}_3^{2-}$ is a slightly weaker acid than H_2PO_4^- (p $K_{a1}^c = 6.13\pm0.04$).

The above interpretation was verified through a direct study of the kinetics of formation of $\text{HO}_3\text{POCrO}_3^{2-}$ 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 $\text{HO}_3\text{POCrO}_3^{2-}$ (pH ≤ 5 , I = 3.0 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 $BCrO_3$ 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 $\rm HCO_3^-/\rm CO_3^{2-}$ 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 hydrolvsed much more rapidly than it is formed. This is certainly a possibility since the H⁺- and OH⁻-catalysed pathways shown here for HO₃POCrO₃ 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 BCrO₃ species (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 $Cr_2O_7^{2-}$ (**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 **B**.

^{*} This species gives rise to a 31 P n.m.r. signal at $3 \cdot 20$ ppm (relative to H₃PO₄ external reference) in aqueous solutions containing $16 \cdot 7\%$ D₂O, $I = 1 \cdot 0$ M, 25° C.

[†] Where comparison is possible good agreement is seen between rate constants determined in the two studies, e.g. $k_{\rm H} = 1.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in the present work compared to $k_{\rm H} = 2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ 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.