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^{17}O NMR Study of Chromium(VI) Ions in Water

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Abstract: A mathematical model for oxygen exchange out of labeled (e.g., ^{17}O) Na_2CrO_4 into solvent H_2O according to the dimerization reaction $2CrO_4^{2-} + 2H^+ \rightleftharpoons (1/K_{a(HCrO_4^-)})\ 2HCrO_4^- \rightleftharpoons (\alpha/\beta)\ Cr_2O_7^{2-} + H_2O$ is described. Two rates of isotopic change are identified: (1) a rapid change intimately associated with the attainment of chemical equilibrium, but not identical with it (rate constants ν_1 and ν_2, respectively), in which the fractional label in monomeric $HCrO_4^- + CrO_4^{2-}$ (p) decreases more rapidly than that in the dimer $Cr_2O_7^{2-}$ (q), i.e. $\dot{p} > \dot{q}$, followed by (2) a slower decrease in both ($\dot{q} > \dot{p}$) until isotopic equilibrium with the solvent is established, $p = q = r$ (rate constant ν_3). Visible−UV and ^{17}O NMR spectra have been used to characterize the elusive $HCrO_4^-$ ion. Vibrational fine structure is seen in the visible spectrum (C_{3v} symmetry), and integration of the monomeric ($HCrO_4^- + CrO_4^{2-}$) ^{17}O absorption agrees with only four O atoms in $HCrO_4^-$. A pH-dependent shift to higher frequency ($\delta_{CrO_4^{2-}} = 812$ ppm; $\delta_{HCrO_4^-} = 860$ ppm) is used to give $pK_{a(HCrO_4^-)} = 5.80$ ($I = 1.0$ M, 25 °C), and comparisons with the integrated $Cr_2O_7^{2-}$ signal ($\delta_{Cr_2O_7^{2-}} = 1115$ ppm) give K_d's for dimerization ($= \alpha/\beta$) of 81 M^{-1} ($I = 1.0$ M) and 132 M^{-1} ($I = 6.0$ M), at 25 °C. Dimerization and hydrolytic rate constants (α and β) have been obtained under the conditions of the ^{17}O exchange experiments; they are shown to contain spontaneous, buffer, and $[H^+]$ and $[OH^-]$ contributions in agreement with earlier investigations. ^{17}O exchange out of enriched Na_2CrO_4 has been followed in aqueous solutions over the concentration range 0.01−2.0 M and over the pH range 6.38−13.0 at 25 °C and constant ionic strength ($I = 1.0, 6.0$). The dimerization reaction (eq 1) contributes only at the highest Cr(VI) concentration (2.0 M), and then only slightly (i.e., ∼10% at pH 7.3). The rate data have been interpreted in terms of the direct exchange paths $Cr^{17}O_4^{2-} + H_2O \rightarrow (k_1)\ Cr^{17}O_3O^{2-} + H_2{}^{17}O$; $HCr^{17}O_4^- + H_2O \rightarrow (k_2)\ HCr^{17}O_3O^- + H_2{}^{17}O$; $H_2Cr^{17}O_4 + H_2O \rightarrow (k_3)\ H_2Cr^{17}O_3O + H_2{}^{17}O$; $Cr_2{}^{17}O_7^{2-} + H_2O \rightarrow (k_4)\ Cr_2{}^{17}O_6O^{2-} + H_2{}^{17}O$, with rate constants $k_1 = 7.2 \times 10^{-8}\ M^{-1}\ s^{-1}$, $k_2 = 7.6 \times 10^{-4}\ M^{-1}\ s^{-1}$, $k_3 = 1.7 \times 10^{5}\ M^{-1}\ s^{-1}$ ($I = 1.0$ M, 25 °C), and $k_4 = 4.1 \times 10^{-3}\ M^{-1}\ s^{-1}$ ($I = 6.0$ M, 25 °C). The monomeric paths (but not the rate constants) agree with those found in an earlier study, but that involving $Cr_2O_7^{2-}$ is new. Rate constants for ^{17}O exchange are compared with those of other substitution reactions of $HCrO_4^-$ and $Cr_2O_7^{2-}$.

Introduction

We have become interested in Cr(VI) as it applies to its mutagenic and carcinogenic properties.[1] It is likely, in our view, that oxidation of thiolic substrates begins with substitution at the Cr(VI) center so that the O lability of Cr(VI) species in aqueous solution is important to establish. The rates and mechanisms of O exchange between water and CrO_4^{2-}, $HCrO_4^-$, H_2CrO_4, and $Cr_2O_7^{2-}$ remain uncertain or unknown.[2] There have been six previous studies, most making use of ^{18}O tracers. Some comment on these is appropriate.

Mills[3] developed an ingenious method for following exchange from isotopically normal Cr(VI) species into ^{18}O-depleted H_2O, whereby he measured the solvent ^{18}O content by timing the fall of drops of H_2O distillate through *m*-fluorotoluene maintained at constant temperature (19.33 °C). Very high Cr(VI) concentrations were used (2.1−5.4 M). Exchange was found to be complete in the time of the first analysis with CrO_3 and more rapid than could be estimated using known rate constants for the dimerization−hydrolysis reaction

$$2HCr^{17}O_4^- \underset{\beta}{\overset{\alpha}{\rightleftarrows}} Cr_2{}^{17}O_7^{2-} + H_2{}^{17}O \qquad (1)$$

when Na_2CrO_4 was used. Mills suggested[4] that dissociative dehydration of H_2CrO_4 was responsible, viz.

$$HCr^{17}O_4^- + H^+ \rightleftharpoons H_2Cr^{17}O_4 \rightleftarrows Cr^{17}O_3 + H_2{}^{17}O \qquad (2)$$

Subsequently, Baloga and Earley[5] used ^{18}O-enriched Li_2CrO_4 (2.68 atom %) and normal H_2O containing $HClO_4$ or LiOH ($I = 1.0$ M). Exchange was monitored by mass spectrometric analysis of O_2 liberated by heating $BaCrO_4$ recovered from the reaction mixture following addition of Ba^{2+} at various times. Much lower Cr(VI) concentrations were used (0.014−0.3 M), and it was found that exchange into CrO_4^{2-} was slow ($1.2 \times 10^{-5}\ s^{-1}$ at 25 °C) and Cr(VI) concentration independent. At pH 7.20, exchange was faster with a second-order dependence on [Cr(VI)]. This latter exchange was attributed to a $k_D[Cr_2O_7^{2-}]$ term in the rate law, with k_D being equated with the hydrolysis rate constant β of eq 1. At Cr(VI) concentrations greater than ∼0.1 M an additional higher-order term in [Cr(VI)] was also noted. Holyer and Baldwin[6] examined in detail this higher concentration condition (1.0−2.68 M), again using H_2O distillates, but this time using mass spectrometric analysis of equilibrated CO_2. They found a [Cr(VI)]-independent rate ($7 \times 10^{-7}\ s^{-1}$, 25 °C) in alkaline solution, and a second-order dependence on [Cr(VI)] with an approaching second-order dependence on $[H^+]$ at pH < 10. This data was once again related to the equilibrium process of eq 1, with the additional pathway

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[1] Standeven, A. S.; Wetterhahn, K. E. *J. Am. Coll. Toxicol.* **1989**, *8*, 1275. Brauer, S. L.; Wetterhahn, K. E. *J. Am. Chem. Soc.* **1991**, *113*, 3001.

[2] Taube, H. *Rec. Chem. Prog.* **1956**, *17*, 25. Stranks, D. R.; Wilkins, R. G. *Chem. Rev.* **1957**, *57*, 743. Myers, O. E.; Prestwood, R. J. In *Radioactivity Applied to Chemistry*; Wahl, A. C., Bonner, N. A., Eds.; Wiley: New York, 1951; Chapter 1. Gamsjäger, H.; Murmann, R. K. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 317.

[3] Mills, G. A. *J. Am. Chem. Soc.* **1940**, *62*, 2833.

[4] The elegance and significance of this early study has not, in our view, been properly recognized by subsequent investigators.

[5] Baloga, M. R.; Earley, J. E. *J. Phys. Chem.* **1963**, *67*, 964.

[6] Holyer, R. H.; Baldwin, H. W. *Can. J. Chem.* **1967**, *45*, 413.

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$$HCr^{17}O_4^{\ -} + Cr^{17}O_4^{\ 2-} \rightleftarrows Cr_2^{\ 17}O_7^{\ 2-} + {}^{17}OH^- \qquad (3)$$

being used to take care of the less than second-order term in $[H^+]$. Mak[7] examined exchange in more acidic solution (pH 4.5−8.4) using a flow method to mix and then quench (as $BaCrO_4$) the reactants. He found much faster rates (reaction times varied from 0.03 to 0.5 s) with a second-order dependence on [Cr(VI)] (at pH 8.4−7.0) turning into a third-order dependence as the acidity increased. No first-order term was found. The second-order term was assigned to dimerization as before, and the third-order term to the processes

$$Cr_2^{\ 17}O_7^{\ 2-} + HCr^{17}O_4^{\ -} \rightleftarrows Cr_3^{\ 17}O_{10}^{\ 2-} + {}^{17}OH^- \qquad (4)$$

and

$$HCr_2^{\ 17}O_7^{\ -} + HCr^{17}O_4^{\ -} \rightleftarrows Cr_3^{\ 17}O_{10}^{\ 2-} + H_2^{\ 17}O \qquad (5)$$

depending on reaction pH. Such processes bear some relationship to the much earlier ^{17}O line broadening study of Figgis, Kidd, and Nyholm[8] (∼4 M [Cr(VI)]), who suggested fast ($k = 2.3 \times 10^3$ $M^{-1}\ s^{-1}$, 27 °C) self-exchange between monomer and dimer in alkaline solution without involvement of solvent:

$$Cr^{17}O_4^{\ 2-} + O_3CrOCrO_3^{\ 2-} \overset{k}{\rightleftarrows} {}^{17}O_3Cr^{17}OCrO_3^{\ 2-} + CrO_4^{\ 2-} \qquad (6)$$

Finally, in the most recent study, where aqueous Ba^{2+} was used to precipitate CrO_4^{2-}, Okumura and co-workers[9] found only a first-order dependence on [Cr(VI)] at low concentrations (0.036−0.14 M) irrespective of pH (12−7.2), which they attributed to the direct pathways 7−9. At higher concentrations (up to 0.96 M), increasing

$$Cr^{17}O_4^{\ 2-} + H_2O \rightarrow Cr^{17}O_3O^{2-} + H_2^{\ 17}O \qquad (7)$$

$$HCr^{17}O_4^{\ -} + H_2O \rightarrow HCr^{17}O_3O^- + H_2^{\ 17}O \qquad (8)$$

$$HCr^{17}O_4^{\ -} + H^+ + H_2O \rightarrow HCr^{17}O_3O^- + H^+ + H_2^{\ 17}O \qquad (9)$$

contributions from second-order, and higher-order, terms were found which they attributed to the dimerization processes of eqs 1 and 3 and to a CrO_4^{2-}-assisted general base catalyzed dimerization process. The direct pathways (eqs 7−9) agree with Mills' early observations,[3] but Okumura suggested, on the basis of a low activation energy (25.5 kJ mol^{-1}), that synchronous water displacement was responsible rather than hydration of the intermediate CrO_3 species.

Overall, the above studies show discrepancies both in observed rates and in experimental rate laws. This may be due in part to the method of analysis. It has long been known that precipitation methods can lead to irregular and often spurious results.[10] Indeed Okumura[9] refers to precipitation-induced exchange into $BaCrO_4$ at pH < 8. Furthermore, adjustment of solution pH to 9 immediately prior to precipitation necessarily involves additional exchange into any $Cr_2O_7^{2-}$ (by hydrolysis), and this becomes increasingly important as the Cr(VI) concentration increases. Distillation procedures also lead to isotopic fractionation. Clearly an *in situ* method of analysis is called for. But the dimerization process of eq 1 must lead to exchange, although the correct methodology for interpreting this for the various Cr(VI) species is not currently available.[11,12]

We decided to use ^{17}O NMR to follow exchange.[13] This gives *in situ* detection, and the separate signals for $Cr_2O_7^{2-}$ (two types of O), $HCrO_4^- + CrO_4^{2-}$, and H_2O[14,15] allow a choice of reagent to follow. Also, the data can be readily analyzed for acidity ($K_{a(HCrO_4^-)}$) and dimerization (K_d) constants. By using 40% ^{17}O-labeled Cr(VI), acceptable rate data can be obtained every 30 s or so (if necessary), and at low concentration (0.01 M).

Results and Discussion

In part A of this section we set up the theory for exchange via dimerization; in part B we give equilibrium and kinetic data which allow exchange via dimerization to be evaluated; and in part C we give our ^{17}O exchange data and discuss the mechanisms for exchange.

A. Oxygen Exchange via Dimerization. Mathematical models for exchange are available for both simple[16] and complex[17] oxyanion systems, but no treatment has been given for exchange via dimerization starting with an enriched substrate. The following treatment identifies *two* rate processes for a system initially not at equilibrium (i.e., such as when isotopically labeled Na_2CrO_4 is dissolved in normal H_2O). The first is intimately associated with the attainment of *chemical equilibrium*, but is not identical with it, and differs for the various Cr(VI) species ($HCrO_4^- + CrO_4^{2-}$, $Cr_2O_7^{2-}$) and H_2O. The second is the more gradual leakage of isotopic label out of the Cr(VI) species into H_2O.

A1. Reactions to Consider. When sodium chromate (Na_2CrO_4), in which some of the oxygen atoms are isotopically labeled, is dissolved in water (which may also contain a label), equilibration with the solvent may occur via the processes

$$2Cr^{17}O_4^{\ 2-} + 2H^+ \rightleftarrows 2HCr^{17}O_4^{\ -} \rightleftarrows Cr_2^{\ 17}O_7^{\ 2-} + H_2^{\ 17}O$$

For convenience this is coded

$$2X_1 + 2H^+ \rightleftarrows 2X_2 \underset{\beta'}{\overset{\alpha'}{\rightleftarrows}} Y + Z \qquad (10)$$

where, according to context, X_1, X_2, and Y are either labels for, or concentrations of, Cr(VI) oxyanions; Z similarly denotes water, and α' and β' are rate constants. For measurements around neutrality, establishment of the X_1/X_2 equilibrium is fast[18]

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[7] Mak, S. Y. C. Ph. D. Thesis. University of Western Ontario, Canada, 1967.

[8] Figgis, B. N.; Kidd, R. G.; Nyholm, R. S. *Can. J. Chem.* **1965**, *43*, 145.

[9] Okumura, M.; Kitani, M.; Toyomi Y.; Okazaki N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3143.

[10] Anbar, M.; Gutman, S. *Int. J. Appl. Radiat. Isot.* **1959**, *5*, 23.

[11] Mills (ref 3) gives a correct analysis of levels of enrichment into solvent H_2O *following* the establishment of chemical equilibrium but does not consider exchange prior to equilibrium or exchange into the various Cr(VI) species.

[12] Authors of refs 4−6 and 8 have all assumed that the observed second-order rate constant for O exchange can simply be related to the second-order rate constant for dimerization (α, eq 1). However it has long been known that for multiexchange processes involving different species, and different types of O atoms within a particular species (i.e., $Cr_2O_7^{2-}$), that chemical and isotopic exchange processes cannot be directly related; cf. ref 17.

[13] Kintzinger, J.-P. In *NMR* **1981**, *17*, 1.

[14] Figgis, B. N.; Kidd, R. G.; Nyholm, R. S. *Proc. R. Soc. (London)*, **1962**, *A269*, 469.

[15] Kidd, R. G. *Can. J. Chem.* **1967**, *45*, 413.

[16] McKay, H. A. C. *Nature* **1938**, *142*, 997. Harris, G. M. *Trans. Faraday Soc.* **1951**, *47*, 716. Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961; p 192. Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; p 311. Logan, S. R. *J. Chem. Educ.* **1990**, *67*, 371.

[17] Johnston, F. J. In *Radiotracer Techniques and Applications;* Evans, E. A., Muramatsu, M., Eds.; Marcel Dekker: New York, **1977**; Vol. 1, p 405.

[18] Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

compared to the $2X_2$ gives $Y + Z$ reaction, so that

$$X_1[\mathrm{H}^+]/X_2 = \text{constant} = K_\mathrm{a} \tag{11}$$

($\mathrm{p}K_\mathrm{a} = 5.80$, 25.0 °C, $I = 1.0$ M ($\mathrm{NaClO_4}$), cf. part B). In any given experiment the pH will also remain constant so that

$$X_1 = \mu X_2, \quad \mu \equiv K_\mathrm{a}/[\mathrm{H}^+] \tag{12}$$

The effect of chromate on the bichromate−dichromate reaction is therefore that of a buffer. Because of the rapidity of the X_1/X_2 equilibrium, labeled O atoms belonging to these two species will appear together in the NMR spectrum, so that we may combine them into a single variable:

$$X = X_1 + X_2 \tag{13}$$

The simplified scheme then becomes

$$2X \underset{\beta}{\overset{\alpha}{\rightleftarrows}} Y + Z \tag{14}$$

in which α and β are apparent rate constants, which can be related to the true second-order rate constants α′ and β′ via the expressions

$$X_2 = \lambda X, \quad \lambda = 1/(1 + \mu)$$

$$\alpha = \alpha'\lambda^2, \quad \beta = \beta' Z \tag{15}$$

Because the label can occur to varying extents in chromate and bichromate, and to varying extents and locations in dichromate, several subspecies X_i, Y_i of X and Y may be distinguished, and it is possible to follow their evolution via the rate constants α and β.[19] (A comparable approach was used by Mills and Urey to follow ^{18}O incorporation into aqueous $\mathrm{H_2CO_3/CO_2}$).[20] However, it is also possible to develop equations for the direct atom (fraction) transfer of O among X, Y, and Z. This approach is used here (when applied to the $\mathrm{H_2CO_3/CO_2/H_2O}$ system, it can be shown that this leads to the same rate equations as developed by Mills and Urey).[21]

A2. Equations of Chemical Evolution. As the isotopic decay processes depend on the concentrations X and Y, it is essential to know the time dependences of these. The appropriate differential equations are

$$\dot{X} = 2(\beta Y - \alpha X^2)$$

$$\dot{Y} = \alpha X^2 - \beta \mathrm{Y} \tag{16}$$

Since $X + 2Y = X_0$ (starting with $\mathrm{Na_2CrO_4}$ at $t = 0$), elimination gives

$$\dot{X} = -2\alpha(X - a_1)(X + a_2) \tag{17}$$

where

$$a_1 = [(\beta^2 + 8\alpha\beta X_0)^{1/2} - \beta]/4\alpha \tag{18}$$

$$a_2 = [(\beta^2 + 8\alpha\beta X_0)^{1/2} + \beta]/4\alpha$$

If we define a rate constant ν_1 such that

$$\nu_1 = 2\alpha(a_1 + a_2) = (\beta^2 + 8\alpha\beta X_0)^{1/2}$$

then the general solution to eq 17 is

$$X = (a_1 C + a_2 \mathrm{e}^{-\nu_1 t})/(C - \mathrm{e}^{-\nu_1 t}) \tag{19}$$

where C is the constant of integration. Since $X = X_0$ when $t = 0$, then $C = (X_0 + a_2)/(X_0 - a_1)$. If $\alpha X_0/\beta \ll 1$, loss of significance may occur in the calculation of a_1 in eq 18. In such cases the approximation $C \cong (\beta/2\alpha X_0)^2$ is useful.

Equation 19 defines the time dependence of X ($\mathrm{CrO_4}^{2-}$ + $\mathrm{HCrO_4}^{-}$) as chemical equilibrium is being established and approaches a single exponential near equilibrium.[22] The first of eqs 18 guarantees $X_0 > a_1$, and $X \rightarrow a_1$ as $t \rightarrow \infty$ Thus a_1 defines the equilibrium concentration of X. The time dependence of Y follows from $Y = (X_0 - X)/2$.

A3. Equations of Isotopic Evolution. We begin with the following definitions: p = atom fraction of label in $\mathrm{CrO_4}^{2-}$ and $\mathrm{HCrO_4}^{-}$; q = atom fraction of label in $\mathrm{Cr_2O_7}^{2-}$; r = atom fraction of label in $\mathrm{H_2O}$.

$$U = [^{17}\mathrm{O}]_x = 4pX$$

$$V = [^{17}\mathrm{O}]_y = 7qY \tag{20}$$

$$W = [^{17}\mathrm{O}]_z = rZ$$

in which U, V, and W represent concentrations of isotopic label. It is these values which are of use in part C.

The equations of isotopic evolution are[23]

$$\dot{U} = \beta(Y + WY/Z) - 2\alpha UX$$

$$\dot{V} = {}^{7}/_{4}\alpha \mathrm{UX} - \beta V \tag{21}$$

$$\dot{W} = {}^{1}/_{4}\alpha UX - \beta WY/Z$$

These can be derived as follows using eqs 20 to eliminate p, q, and r. The rate of conversion of X into Y is $2\alpha X^2$, so the rate of loss of label from X is $4p(2\alpha X^2) = 2\alpha UX$. At the same time, label is returning to X from Y at a rate $7q\beta Y = \beta V$, and from Z at a rate $r\beta Y = \beta WY/Z$. The first of eqs 21 follows. Similarly, label is being lost from Y to X at a rate βV. When calculating the rate at which label is being received by Y from W, we have to take into account the fact that one oxygen atom (out of eight) is lost to solvent whenever a dichromate ion is formed. Thus the rate of transfer of label from X to Y is $7p\alpha X^2 = 7\alpha UX/4$. The second of eqs 21 is now explained. Finally, the rate of loss of label from the water is $\beta WY/Z$, and the rate of transfer of label from bichromate to water is $(^1/_8)2p\alpha X^2 = \alpha UX/4$. This accounts for the last of eqs 21.

Adding eqs 21 gives the expected conservation law $U + V + W = U_0 + W_0 \cong U_0$.[24]

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[19] Details of this analysis are available on request; they lead to the same rate equations as given here, but are somewhat more lengthy.

[20] Mills, G. A.; Urey, H. C. *J. Am. Chem. Soc.* **1940**, *62*, 1019.

[21] Details available on request.

[22] Bernasconi, C. F. In *Relaxation Kinetics*; Academic Press: New York, 1976; pp 14−15.

[23] That for $\dot{W}$ can be equated to the rate equation developed by Mills (cf. ref 3) following the establishment of chemical equilibrium.

[24] Experimentally W_0 is usually $< U_0$ (e.g., for a 0.03 M solution of 40% ^{17}O-enriched $\mathrm{Na_2CrO_4}$, $U_0 = 0.048$ M; $W_0 = 0.0205$ M for natural abundance $\mathrm{H_2O}$).

Table 1. Chemical Concentrations (*X*), Isotopic Concentrations (*U*), Isotopic Fractions (*p*) for Monomeric Cr(VI) (CrO_4^{2-} + $HCrO_4^-$), and Isotopic Fractions for $Cr_2O_7^{2-}$ (*q*) and H_2O (*r*) Calculated for O Exchange via the Dimerization Mechanism (Eq 1) at pH = 3.00 ($\alpha = 402.5\ M^{-1}\ s^{-1}$, $\beta = 5.03\ s^{-1}$; $X_0 = 0.10$ M, $p_0 = 0.40$; $Y_0 = 0.00$ M; $Z_0 = 55.5$ M, $r_0 = 0.037\%$), *T* = 25 °C, and *I* = 1.0 M

t/s	*X*/M	*U*/M	*p*	*p*/*q*	*r*
0.0000	0.100	0.160	0.400	1.000	0.000 37
0.0001	0.099	0.159	0.400	1.000	0.000 37
0.0100	0.056	0.090	0.399	0.998	0.000 53
0.0200	0.041	0.064	0.396	0.993	0.000 60
0.0300	0.033	0.052	0.392	0.985	0.000 63
0.0400	0.029	0.045	0.388	0.975	0.000 66
0.0500	0.026	0.041	0.383	0.965	0.000 68
0.0600	0.025	0.038	0.378	0.955	0.000 70
0.0700	0.024	0.036	0.373	0.946	0.000 71
0.0800	0.023	0.034	0.369	0.939	0.000 73
0.0900	0.023	0.033	0.365	0.932	0.000 74
0.1000	0.023	0.033	0.361	0.926	0.000 76
0.20	0.022	0.030	0.337	0.904	0.000 88
0.30	0.022	0.028	0.320	0.901	0.001 00
0.40	0.022	0.027	0.304	0.901	0.001 11
0.50	0.022	0.026	0.290	0.901	0.001 21
0.60	0.022	0.024	0.275	0.901	0.001 31
0.70	0.022	0.023	0.262	0.901	0.001 41
0.80	0.022	0.022	0.249	0.900	0.001 50
0.90	0.022	0.021	0.237	0.901	0.001 58
1.00	0.022	0.020	0.226	0.901	0.001 66
2	0.022	0.012	0.138	0.902	0.002 28
3	0.022	0.007	0.084	0.903	0.002 66
4	0.022	0.005	0.052	0.905	0.002 88
5	0.022	0.003	0.033	0.909	0.003 02
6	0.022	0.002	0.021	0.914	0.003 10
7	0.022	0.001	0.014	0.921	0.003 15
8	0.022	0.001	0.010	0.931	0.003 18
9	0.022	0.001	0.007	0.942	0.003 20
10	0.022	0.000	0.006	0.955	0.003 21
20	0.022	0.000	0.003	0.999	0.003 23
30	0.022	0.000	0.003	1.000	0.003 23
40	0.022	0.000	0.003	1.000	0.003 23
50	0.022	0.000	0.003	1.000	0.003 23

Alternatively eqs 21 may be expressed in terms of atom fractions

$$\dot{p} = (\beta Y/4X)(7q + r - 8p)$$

$$\dot{q} = (\alpha X^2/Y)(p - q) \tag{22}$$

$$\dot{r} = (\alpha X^2 p - \beta Y r)/Z$$

Equations 21 hold at all times, but for evaluation purposes that for $\dot{q}$ in eq 22 requires a limit to be taken when $Y \to 0$, $t \to 0$.

A4. Numerical Evaluations of Isotopic Exchange. As stated above we can use exact solutions for *X* and *Y* (cf. section A2) to carry out numerical integrations of the nonlinear eqs 21 or 22. For $\dot{q}$ in eq 22, we need to find the limit as $t \to 0$ and this can readily be done by expanding the variables in powers of *t*. The most relevant results are

$$p = p_0 - p_2 t^2 - ...$$

$$q = p_0 - p_2 t^{2/3} - ... \tag{23}$$

in which p_2 takes the value $\alpha\beta X_0\ (p_0 - r_0)/8$. Integration of system 22 and insertion into eqs 20 then leads to values of *U*, *V*, and *W*.

Numerical data for one set of conditions are listed in Table 1. It can be seen that *p* and *q* start from the same initial value p_0, but over time decrease, with *p* diminishing more rapidly than *q* at first. This results from the fact that in the forward dimerization reaction $Cr_2O_7^{2-}$ (and H_2O) is produced with the same fractional label as $HCrO_4^-$, whereas in the reverse hydrolysis reaction solvent, with a lesser ^{17}O content, is introduced causing an immediate reduction in *p*. It can be shown that the *p*/*q* ratio will never fall below the value 7/8. Data for *U* are shown graphically in Figure 1. The initial change in *U* closely follows that for chemical change (*X*), but because *p* is also decreasing, slowly at first, the correspondence is never exact. Thus changes in isotopic concentration never parallel those for chemical change.

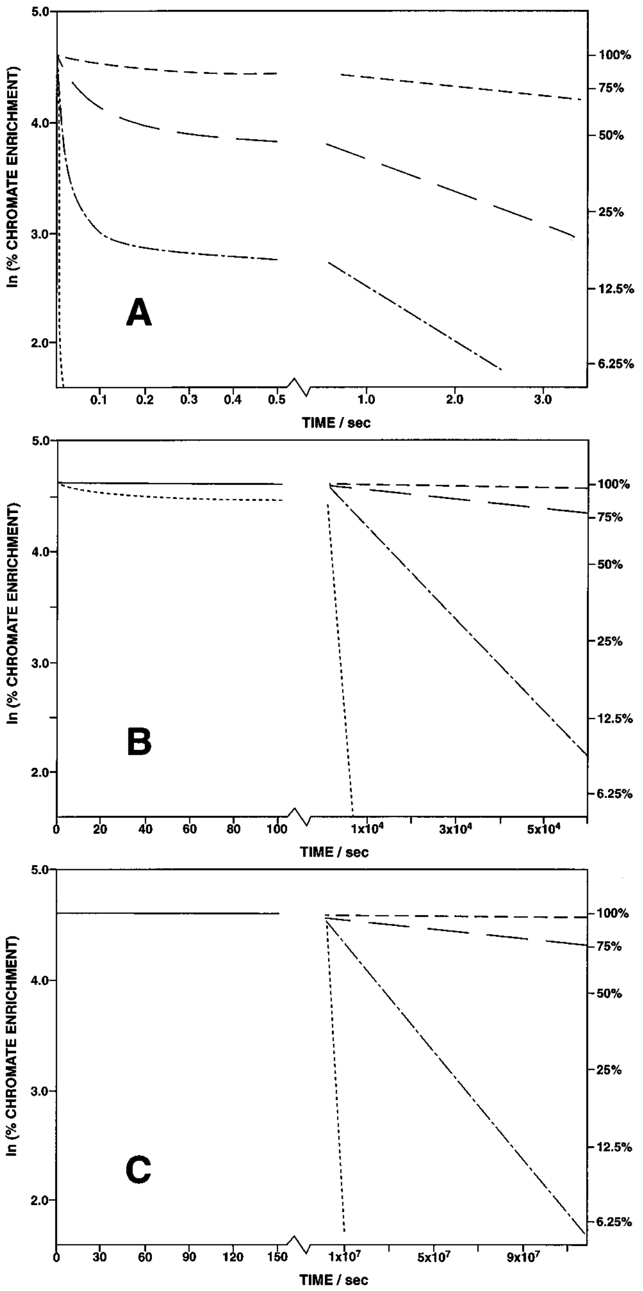

Figure 1. Rates of loss of oxygen label (i.e., ^{17}O or ^{18}O) from monomeric chromate into water (unlabeled) at three pHs (A, 3.0; B, 7.3; C, 9.0) and four Cr(VI) concentrations [(— — —) 0.001 M, (—) 0.01 M, (– - –) 0.10 M, and (---) 2.0 M] calculated assuming that exchange occurs via dimerization (eq 1). Rate constants (α and β) are given in Table 1.

A5. Evaluation of Rate Constants for Isotopic Exchange. Isotopic equilibrium will normally be far from complete when chemical equilibrium has been established. Under this condition an isotopic imbalance between all three O-containing species

Table 2. Chemical and Isotopic Exchange Rate Constants

Cr(VI)/M	pH	α^a/M^{-1} s^{-1}	β^c/s^{-1}	ν_1/s^{-1}	ν_2/s^{-1}	ν_3/s^{-1}
0.001	3.0	402.5	5.03	6.44	5.66	7.82×10^{-2}
0.01				13.7	9.05	0.30
0.10				40.5	22.3	0.50
2.0		674^b	5.03	232	118	0.68
0.001	6.0	2.90	0.036	3.74×10^{-2}	3.66×10^{-2}	8.30×10^{-5}
0.01				4.78×10^{-2}	4.13×10^{-2}	6.44×10^{-4}
0.10				0.106	6.86×10^{-2}	2.30×10^{-3}
2.0		4.85^b	0.036	0.396	0.212	4.31×10^{-3}
0.001	7.3	2.52	0.032	3.20×10^{-2}	3.20×10^{-2}	4.14×10^{-7}
0.01				3.21×10^{-2}	3.20×10^{-2}	4.13×10^{-6}
0.10				3.27×10^{-2}	3.23×10^{-2}	4.09×10^{-5}
2.0		4.23^b	0.032	3.91×10^{-2}	3.51×10^{-2}	4.61×10^{-4}
0.001	9.0	3.50	0.0436	4.36×10^{-2}	4.36×10^{-2}	2.41×10^{-10}
0.01				4.36×10^{-2}	4.36×10^{-2}	2.41×10^{-9}
0.10				4.36×10^{-2}	4.36×10^{-2}	2.43×10^{-8}
2.0		5.86^b	0.0436	4.36×10^{-2}	4.36×10^{-2}	3.20×10^{-7}

[a] $\alpha = 2.5\ (4.0 \times 10^5)a_{\mathrm{H^+}} + (1.0 \times 10^5)a_{\mathrm{OH^-}}$; $K_d = 80$ M^{-1} ($I = 1.0$ M). [b] $\alpha = 4.185 + (6.70 \times 10^5)a_{\mathrm{H^+}} + (1.69 \times 10^5)a_{\mathrm{OH^-}}$; $K_d = 132$ M^{-1} ($I = 6.0$ M). [c] $\beta = \alpha/K_d$.

still exists, $q > p \gg r$; p and q are normally still far from their equilibrium values, $p = q = r$.

Once chemical equilibrium has been established, X and Y become constant (values a_1 and $\alpha a_1^2/\beta$, respectively; cf. section A2), making eqs 21 and 22 linear and homogeneous with constant coefficients; viz. for (22)

$$\dot{p} = (\alpha a_1/4)(7q + r - 8p)$$

$$\dot{q} = \beta(p - q) \qquad (24)$$

$$\dot{r} = (\alpha a_1^2/Z)(p - r)$$

Standard matrix methods may then be applied for their solution. Equations 24 take the form $\dot{x} = \mathbf{A}x$, where

$$\mathbf{A} = \begin{bmatrix} -8A_1 & 7A_1 & A_1 \\ A_2 & -A_2 & 0 \\ A_3 & 0 & -A_3 \end{bmatrix}$$

with $A_1 = \alpha a_1/4$, $A_2 = \beta$, and $A_3 = \alpha a_1^2/Z$. Their general solution, determined by the matrix coefficients, is

$$x = C_1\epsilon_1 + C_2\epsilon_2 e^{-\nu_2 t} + C_3\epsilon_3 e^{-\nu_3 t} \qquad (25)$$

where ν_2 and ν_3 are negatives of the non-zero eigenvalues of $\mathbf{A}$, ϵ_i are the corresponding eigenvectors, and C_i are the constants of integration (the eigenvalue corresponding to eigenvector ϵ_1 can be shown to be 0). It is clear that there are two rates of isotopic evolution, with the rate constants ν_2 and ν_3 being solutions to the quadratic

$$\nu^2 - (8A_1 + A_2 + A_3)\nu + (A_1A_2 + A_2A_3 + 7A_1A_3) = 0 \quad (26)$$

We have chosen $\nu_3 < \nu_2$ such that ν_3 dominates at large t. Table 2 lists ν_2 and ν_3 values, as well as ν_1 for chemical evolution, at four pH values and four Cr(VI) concentrations.

It can be seen that ν_2 differs usefully from ν_1 only at low pH and high [Cr(VI)]. In part C of this paper, because of the experimental method employed, we will only be concerned with ν_3. This is correctly represented by the McKay equation[25]

$$\ln\{([^{17}\mathrm{O}]_t - [^{17}\mathrm{O}]_\infty)/([^{17}\mathrm{O}]_0 - [^{17}\mathrm{O}]_\infty)\} = -\nu_3 t \quad (27)$$

and dominates overall exchange at pH values > 7. Table 2 shows ν_3 to have a first-order dependence on [CrVI] at pH 9.0 and 7.3 (i.e., it represents a second-order rate constant) but is beginning to approach independence in [Cr(VI)] at pH 3.0.

B. Equilibrium and Rate Constants. Early potentiometric[26−29] and spectrophotometric[28,30] studies suggested the existence of monomeric $HCrO_4^-$ in neutral and acidic aqueous solution, and more recent measurements using similar methods have confirmed this.[31−33] However its existence has also been disputed on the grounds that an absorption, expected at 880 cm^{-1} in the Raman spectrum, is not seen.[34,35] This uncertainty has found its way into the recent review literature.[36] In this section we give additional spectral evidence for the existence of $HCrO_4^-$, and ^{17}O NMR data relating to its properties, as well as kinetic data for its conversion into $Cr_2O_7^{2-}$ (α and β, eq 1) under the conditions used in the O-exchange study (part C).

B1. Properties of $HCrO_4^-$. Figure 2A gives the visible spectrum of a very dilute (5.2×10^{-2} mM) solution of Na_2CrO_4 at pH 9.98 (a) and 3.05 (b), $I = 1.0$ M, $NaClO_4$, 25 °C. The two clearly differ, but both obey Beer's Law over a 10-fold concentration range about this concentration. At concentrations greater than 1 mM, Beer's law is still obeyed for the pH 9.98 data, but at pH 3.05, Beer's law is not followed due to increasing polymerization (e.g., $Cr_2O_7^{2-}$ formation). The 5.2×10^{-2} mM spectrum shows a pH independence between 11.0 and 7.5 (Figure 2A(**a**)) and between 3.5 and 1.5 (Figure 2A-(**b**)), but between pH 7.5 and 4.0, titration with 1 M $HClO_4$ (microliter additions) gave an excellent titration curve (370 nm, inset of Figure 2A) corresponding to the addition of one H$^+$ per Cr(VI), giving $K_a = (1.51 \pm 0.10) \times 10^{-6}$ M (pK_a = 5.82) under this 1.0 M $NaClO_4$ condition (25 °C). Increasing the Cr(VI) concentration by a factor of 4 gave an identical titration curve. Titration in 3 M $NaClO_4$ gave $K_a = (2.8 \pm 0.2) \times 10^{-6}$ M (pK_a = 5.55) and in 6 M $NaClO_4$ $K_a = (3.2 \pm 0.2) \times 10^{-6}$ M (pK_a = 5.49). Such data demonstrate an electrolyte, but not a Cr(VI) concentration, dependence. Provided CrO_4^{2-} is

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[25] McKay, H. A. C. *Nature* **1938**, *142*, 997. Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961; p 192. Logan, S. R. *J. Chem. Educ.* **1990**, *67*, 371.

[26] Neuss, J. D.; Rieman, W. *J. Am. Chem. Soc.* **1934**, *56*, 2238.

[27] Davies, W. G.; Prue, J. E. *Trans. Faraday Soc.* **1955**, *51*, 1045.

[28] Howard, J. R.; Nair, V. S. K.; Nancollas, G. H. *Trans. Faraday Soc.* **1958**, *54*, 1034.

[29] Schwarzenbach, G.; Meir, J. *J. Inorg. Nucl. Chem.* **1958**, *8*, 302.

[30] Tong, J. Y.-P.; King, E. L. *J. Am. Chem. Soc.* **1953**, *75*, 6180.

[31] Sasaki, Y. *Acta Chem. Scand.* **1962**, *16*, 719.

[32] Linge, H. G.; Jones, A. L. *Aust. J. Chem.* **1968**, *21*, 1445.

[33] Palmer, D. A.; Wesolowski, D.; Mesmer, R. E. *J. Soln. Chem.* **1987**, *16*, 443.

[34] Michel, G.; Machinoux, R. *J. Raman. Spectrosc.* **1983**, *14*, 22.

[35] Michel, G.; Cahay, R. J. *J. Raman Spectrosc.* **1986**, *17*, 79.

[36] Cieslak-Golonka M. *Coord. Chem. Rev.* **1991**, *109*, 223.

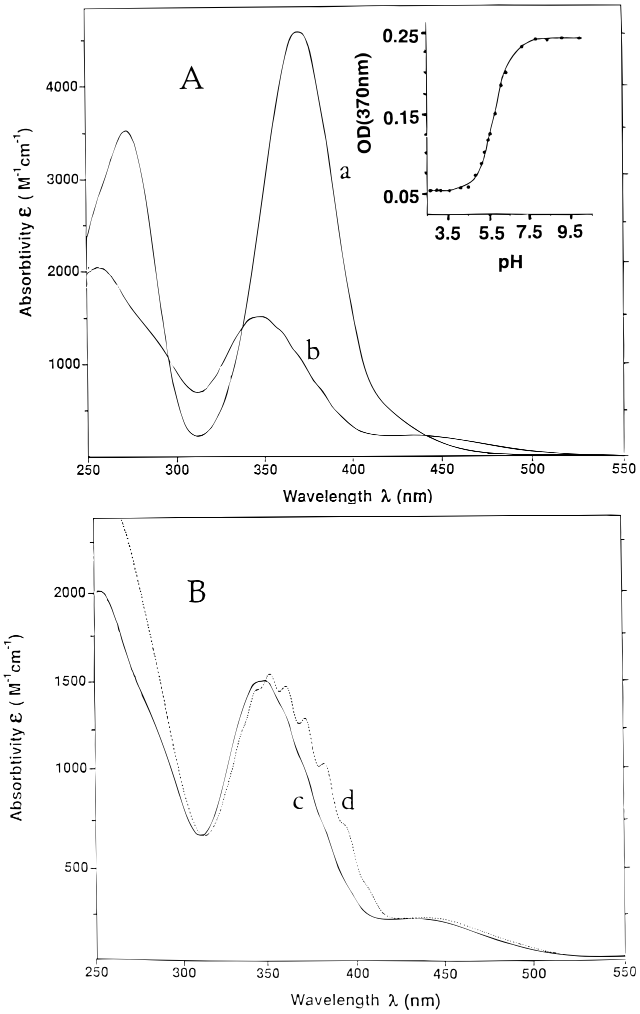

Figure 2. (A) Absorption spectra of 5.16×10^{-2} mM Cr(VI) solutions (1.0 M $NaClO_4$, 25 °C) at (a) pH 9.98 ($\epsilon_{374} = 4570$, $\epsilon_{274} = 3550$), and (b) pH 3.05 ($\epsilon_{348} = 1490$, $\epsilon_{257} = 2010$). Inset gives the pH titration curve. (B) Absorption spectra of acidified 0.208 mM solutions of Cr(VI) in (c) H_2O and (d) CH_3CN containing 2.5% H_2O.

accepted as the species present in alkaline solution eq 28 follows:

$$CrO_4^{2} + H^+ \rightleftharpoons HCrO_4^- \ (1/K_{a(HCrO_4^-)}) \qquad (28)$$

A potentiometric titration (0.01 M Cr(VI), 1.0 M, $NaClO_4$, 25 °C) also showed the addition of one H^+ per Cr(VI) centered at pH 5.72,[37] but its Cr(VI) independence was not established and so distinction from dimerization reaction 1 was not proved. However, earlier potentiometric data by Sasaki[31] obtained at low concentration (0.1, 0.2 mM) clearly establish equilibrium 28 as the correct expression. Table 3 summarizes our K_a values and compares them with those in the literature.

Close examination of the pH 3.05 spectrum, Figure 2B**(c)** shows the presence of substructure in the near-UV (350−400 nm), and this is more apparent when the spectrum is recorded in acetonitrile (2.5% H_2O), Figure 2B**(d)**. Such substructure can be attributed to vibrational bands caused by a change from T_d to C_{3v} symmetry.[38] Similar spectra have been observed for other CrO_3X^- species (X = F, Cl, Br).[39] It was outside the scope of the present investigation to study this in detail, but the asymmetry of the $CrO_3(OH)^-$ ion (compared to CrO_4^{2-}) appears to be established.

Table 3. pK_a and K_d Values (25 °C)[a]

pK_a[b]	K_d/M^{-1} [c]	ref
5.82 (S)	80	this work
	107	48
	77	57 (0.5 M $NaClO_4$)
5.55 (S)		this work (3 M $NaClO_4$)
5.89 (S, P)		31 (3 M $NaClO_4$)
5.49 (S)	132	this work (6 M $NaClO_4$)
5.72 (P)		this work
5.80 (N)	81	this work
5.76 (P)	67	33

[a] $I = 1.0$ M ($NaClO_4$) unless otherwise stated. [b] S = spectrophotometric, P = potentiometric, N = ^{17}O NMR method. [c] $K_d = [Cr_2O_7^{2-}]/[HCrO_4^-]^2$.

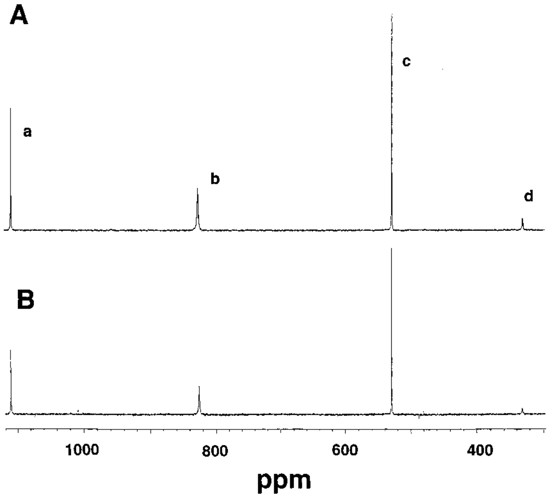

Figure 3. ^{17}O NMR spectra (reference external, MoO_4^{2-}, 529 ppm) of (A) 0.18 M Cr(VI) at pH 6.10 and $I = 1.0$ M ($NaCF_3SO_3$) and (B) 2.00 M Cr(VI) at pH 5.83 and $I = 6.0$ M (solvent enrichment 4%). Signal assignments: (a) $Cr_2O_7^{2-}$ (terminal O), (b) CrO_4^{2-} (+ $HCrO_4^-$), (c) MoO_4^{2-}, (d) $Cr_2O_7^{2-}$ (bridging O).

Unlike visible spectral or potentiometric measurements, an ^{17}O NMR study gives more definitive information since the monomer and dimer can be seen as separate absorptions. Figure 3 gives two such spectra at pH ~ 6 ([Cr(VI)] = 0.18 and 2.0 M) externally referenced to MoO_4^{2-} (529 ppm). The $Cr_2O_7^{2-}$ signals appear at 1115 ppm (terminal) and 335 ppm (bridging), intensity ratio 6:1, and the chemical shift and line width of the 1115 ppm signal was shown to be independent of pH (7.0−3.0) and Cr(VI) concentration (0.02−0.32 M). This means that chemical exchange broadening as suggested by Figgis and coworkers[8] (eq 6) and H^+-catalyzed hydrolysis of $Cr_2O_7^{2-}$ as observed by Jackson and Taube[40] are not important rate processes under these conditions. However the $CrO_4^{2-}/HCrO_4^-$ absorption (820−860 ppm) does show a pH dependence moving to lower frequencies and broadening as the pH is decreased. The field shift can be related to protonation, and line broadening, to T_1 and T_2 relaxation in the $HCrO_4^-$ ion. The latter aspect has been discussed in detail elsewhere.[41] No additional absorptions were seen up to 2.0 M Cr(VI) so that other species, such as $Cr_3O_{10}^{2-}$, are not present in significant amounts under these conditions.

The chemical shift in the $CrO_4^{2-}/HCrO_4^-$ absorption (820−860 ppm) was used to determine the acidity constant of $HCrO_4^-$.

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(37) Brasch, N. E. Ph.D. Thesis, University of Otago, 1993.

(38) Cieslak-Golonka, M.; Bartecki, A. *Bull. Pol. Acad. Chem. Sci.* **1978**, *26*, 53.

(39) Miskowski, V.; Gray, H. B.; Ballhausen, C. K. *Mol. Phys.* **1974**, *28*, 729.

(40) Jackson, J. A.; Taube, H. *J. Phys. Chem.* **1965**, *69*, 1844.

(41) Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Rowan, A. E. *Aust. J. Chem.*, in press.

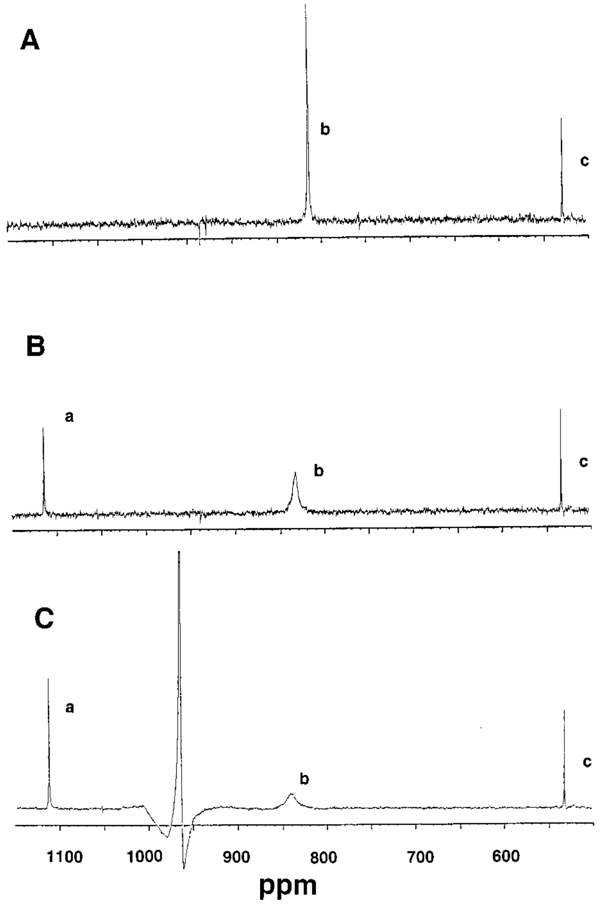

Figure 4. ^{17}O NMR spectra for a solution 0.025 M in Cr(VI) and $I = 1.0$ M ($NaCF_3SO_3$) in 35% $H_2{}^{17}O$: (A) pH = 7.05; (B) pH = 6.05; (C) pH = 5.58 (the peak at ∼970 ppm arises from folding back of the water signal). Signal assignments: (a) $Cr_2O_7{}^{2-}$ (terminal O), (b) $CrO_4{}^{2-}$ + $HCrO_4{}^-$, (c) $MoO_4{}^{2-}$.

Two titrations with CF_3SO_3H were carried out, the first using 0.32 M Na_2CrO_4 in 5% ^{17}O-enriched H_2O ($I = 1.0$ M) and the second using 0.025 M Na_2CrO_4 in 35% ^{17}O-enriched H_2O ($I = 1.0$ M with $NaCF_3SO_3$). Three representative spectra from the second titration are shown in Figure 4, and Table 4 gives more extensive data (cf. supporting information). The observed chemical shift (δ_{obs}) represents the weighted average for $CrO_4{}^{2-}$ ($\delta_{CrO_4{}^{2-}}$) and $HCrO_4{}^-$ (δ_{HCrO_4-}), viz.

$$\delta_{obs} = f_{CrO_4{}^{2-}}\delta_{CrO_4{}^{2-}} + f_{HCrO_4{}^-}\delta_{HCrO_4{}^-} \qquad (29)$$

($f_{CrO_4{}^{2-}}$ and $f_{HCrO_4{}^-}$ represent mole fractions). Incorporation into equilibrium 28 leads to

$$\delta_{obs} = (\delta_{HCrO_4{}^-}a_{H^+} + \delta_{CrO_4{}^{2-}}K_a)/(K_a + a_{H^+}) \qquad (30)$$

in which all quantities except K_a and δ_{HCrO_4-} are known ($\delta_{CrO_4{}^{2-}}$ = 812 ppm was taken as the average of two observations at high pH). It was not possible to observe directly the $HCrO_4{}^-$ ion (δ_{HCrO_4-}) since the signal broadened into the baseline at pH values < 5. Fitting the data to eq 30[42] gave $K_a = 1.58 \times 10^{-6}$M (p$K_a$ = 5.80) and δ_{HCrO_4-} = 860 ppm. This K_a value agrees well with the spectrophotometric value (Table 3).

Information relating to the number of oxygen atoms in $HCrO_4{}^-$ can also be obtained from the areas of the Cr(VI) signals at $[Cr]_T = 0.025$ M (Figure 4) provided it is accepted that $CrO_4{}^{2-}$ contains four,[43] and $Cr_2O_7{}^{2-}$ seven, O atoms. Table 5 lists signal areas obtained at three pH values. The total area (column 4), allowing for the one O atom lost from $Cr_2O_7{}^{2-}$ to H_2O, is essentially constant. If $HCrO_4{}^-$ were present as $H_3CrO_5{}^-$ (i.e., as five-coordinate $CrO_3(OH)(OH_2)^-$), then the combined total area of the pH 5.58 absorptions would be 85.8 units (at this pH some 36% of the combined signal area represents $HCrO_4{}^-$). Within the accuracy of the integration (±5% over the three measurements), the observed total area falls short of this and remains invariant at the three acidities. It is therefore concluded that $HCrO_4{}^-$ is properly represented as containing four bound O atoms.

B2. Dimerization Constant (K_d) and Dimerization Rates (α and β). The separate ^{17}O absorptions provide a direct measure of K_d ($K_d = [Cr_2O_7{}^{2-}]/[HCrO_4{}^-]^2$) once K_a is known. Integration of the $Cr_2O_7{}^{2-}$ and combined monomer ($CrO_4{}^{2-}$ + $HCrO_4{}^-$) signals was carried out at four pH values following titration of 0.18 M Na_2CrO_4 with 2 M CF_3SO_3H in 5% $H_2{}^{17}O$. These data (Table 6, supporting information) give an average K_d value of 81 ± 5 M^{-1} at $I = 1.0$ M ($NaClO_4$) and a value of 132 M^{-1} for the one measurement at $I = 6.0$ M (Na_2SO_4). The former value agrees well with the spectrophotometric value (80 M^{-1}, Table 3), and the latter compares with a reported value of 133 M^{-1} in 3.0 M $NaClO_4$.[44]

Let us now examine the dimerization rates since, in order to compare the observed rates of O exchange (part C) with those calculated from the dimerization equilibrium, it is necessary to know α and β under the same conditions. Forward and reverse rates are given by[45]

$$R_f = \alpha[HCrO_4{}^-]^2$$

$$R_r = \beta[Cr_2O_7{}^{2-}] \qquad (31)$$

with α and β containing both acid[46] and base[47] contributions, viz.

$$\alpha = k_1 + k_2a_{H^+} + k_3a_{OH^-} + k_4[B] + k_5[HA]$$

$$\beta = k_{-1} + k_{-2}a_{H^+} + k_{-3}a_{OH^-} + k_{-4}[B] + k_{-5}[HA] \qquad (32)$$

Activation parameters ($\Delta H^{\ddagger}$,[48] $\Delta S^{\ddagger}$,[49] and $\Delta V^{\ddagger}$ [50]) have been obtained for some of these pathways.

Rate data (k_{obs}) for the approach to equilibrium in acid solution (pH 2−3) were obtained by rapidly mixing Na_2CrO_4 and $HClO_4$ solutions and following the absorbance change on a stopped-flow spectrophotometer. Under this condition only the H^+-catalyzed pathway is important,[48−51] viz. $\alpha = k_2a_{H^+}$ and $\beta = k_{-2}a_{H^+}$, and variation in the observed first-order rate

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[42] Nonlinear least-squares analysis was used.

[43] A crystal structure of K_2CrO_4 shows four O atoms tetrahedrally disposed about Cr. Cf.: Siddiqi, K. S.; Siddiqi, M. R. H.; Khan, P.; Khan, S.; Zaidi, S. A. A. *Synth. React. Inorg. Metal-Org. Chem.* **1982**, *12*, 521.

[44] Arnek, R.; Johansson, S. R. *Acta Chem. Scand.* **1972**, *26*, 2903.

[45] Swinehart, J. H.; Castellan, G. W. *Inorg. Chem.* **1964**, *3*, 278. Swinehart, J. H. *J. Chem. Educ.* **1967**, *44*, 524.

[46] Baharad, R.; Perlmutter-Hayman, B.; Wolff, M. A. *J. Phys. Chem.* **1969**, *73*, 4391.

[47] Perlmutter-Hayman, B.; Wolff, M. A. *J. Phys. Chem.* **1967**, *71*, 1416.

[48] Pladziewicz, J. R.; Espenson, J. H. *Inorg. Chem.* **1971**, *10*, 634.

[49] Moore, P.; Kettle, S. F. A.; Wilkins, R. G. *Inorg. Chem.* **1966**, *5*, 220.

[50] Moore, P.; Ducommun, Y.; Nichols, P. J.; Merbach, A. E. *Helv. Chim. Acta* **1983**, *66*, 2445.

[51] Fischer, R.; Bye, J. *Bull. Soc. Chim. Fr.* **1964**, 2920.

Table 5. ^{17}O NMR Results[a] [Analysis of Peak Areas in Figure 4 ([Cr(VI)] = 0.025 M; I = 1.0 M ($NaCF_3SO_3$); 25 °C)]

	$CrO_4^{2-} + HCrO_4^-$		$Cr_2O_7^{2-}$				$(CrO_4^{2-}+HCrO_4^-)$	$(CrO_4^{2-}+HCrO_4^-)$	
pH	ppm	$(area)_{obs}$[b]	ppm[c]	$(area)_{obs}$[b]	$(area)_{obs} \times {}^8/_6$[c]	total area	% $(area)_{obs}$[d]	% $(area)_{calc}$[e]	% $HCrO_4^-$ [f]
7.05	817	75.1		0	0	75.1	100	99	5.0
6.05	832	54.7	1115	14.7	19.6	74.3	73.6	77.2	37
5.58	842	46.3	1115	24.1	32.1	78.4	59.1	60.6	63.5

[a] Areas obtained by instrument integration (average of three); arbitrary units. [b] Observed area corrected using standard (external) MoO_4^{2-} absorption. [c] Terminal O absorption. The factor $^8/_6$ allows for loss of one oxygen to solvent and one to bridging oxygen (335 ppm signal not shown) on forming $Cr_2O_7^{2-}$ from two $HCrO_4^-$ units. [d] Observed % area ($CrO_4^{2-} + HCrO_4^-$). [e] Calculated % area ($CrO_4^{2-} + HCrO_4^-$) based on pK_a = 5.82, $K_d = 80$ M^{-1}, and four O atoms in both CrO_4^{2-} and $HCrO_4^-$, i.e. % $(area)_{calc} = 100\,(4[CrO_4^{2-}] + 4[HCrO_4^-])/(4[CrO_4^{2-}] + 4[HCrO_4^-] + 6[Cr_2O_7^{2-}])$. $[Cr]_T = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] = 0.025$ M. [f] Calculated % $HCrO_4^-$ in ($CrO_4^{2-} + HCrO_4^-$) absorption, based on pK_a = 5.82.

constant is given by

$$k_{obs} = k_{-2}a_{H^+} + 4k_2a_{H^+}[HCrO_4^-] \quad (33)$$

$[HCrO_4^-]$ can be expressed as

$$[HCrO_4^-] = (-1 + (1 + 8(k_2/k_{-2})[Cr_T]^{1/2})/4(k_2/k_{-2}) \quad (34)$$

where $[Cr_T]$ represents the total chromium concentration (i.e., $[Cr_T] = 2[Cr_2O_7^{2-}] + [HCrO_4^-]$). Rate data (Table 7, supporting information) were fitted to eqs 33 and 34 giving $k_2 = 4.01 \times 10^5$ M^{-2} s^{-1}, $k_{-2} = 5.04 \times 10^3$ M^{-1} s^{-1}, and $K_d = k_2/k_{-2} = 80$ M^{-1}. The k_2 and k_{-2} values are in reasonable agreement with those of Pladziewicz and Espenson,[48] obtained under similar conditions (1 M $LiClO_4$, $k_2 = 6.33 \times 10^5$ M^{-2} s^{-1}, $k_{-2} = 6.35 \times 10^3$ M^{-1} s^{-1}).

The reaction in neutral solution (pH 6−7) also contains contributions from the spontaneous pathways k_1 and k_{-1} so that $\alpha = k_1 + k_2a_{H^+}$ and $\beta = k_{-1} + k_{-2}a_{H^+}$. Under this condition the approach to equilibrium is a relaxation process[22] with first-order rate constants given by

$$k_{obs} = k_{-1} + k_{-2}a_{H^+} + 4(k_1 + k_2a_{H^+})[HCrO_4^-] \quad (35)$$

where

$$[HCrO_4^-] = (-(1 + K_a/a_{H^+}) + ((1 + K_a/a_{H^+})^2 + 8K_d[Cr_T])^{1/2})/4K_d \quad (36)$$

($[Cr_T] = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}]$). Rate data under these conditions were obtained by mixing Na_2CrO_4 and $Na_2Cr_2O_7$ plus indicator solutions and following the absorbance increase due to the indicator. The wavelength chosen depended on the indicator used, and this in turn depended on the solution pH. Table 8 lists data (supporting information), and the best fit to eqs 35 and 36 was obtained using $k_1 = 2.4$ M^{-1} s^{-1} and $k_{-1} = 0.030$ s^{-1}.

In alkaline solution only the hydrolysis term $k_{-3}a_{OH^-}$ is important. This takes on a value of 1.26×10^3 M^{-1} s^{-1}, (c.f. Table 9, supporting information).

Buffers were used in the O-exchange experiments to maintain pH, and it was necessary to determine their contribution to eqs 32. These data are rather extensive and are given in their entirety elsewhere.[37] Direct nucleophilic catalysis in the hydrolysis of $Cr_2O_7^{2-}$ has been reported for TRIS[52] and HPO_4^{2-}.[53] Table 10 summarizes rate constants for buffer catalysis; these are used in part C below.

Table 10. Rate Constants (k_{-4}) for Buffer-Catalyzed Hydrolysis of $Cr_2O_7^{2-}$ (I = 1.0 M ($NaClO_4$), 25 °C)

buffer	buffer pK_a[a]	k_4/M^{-1} s^{-1}
CAPS	10.57	76
CHES	9.59[b]	47
DABCO	9.29	4.35×10^3
TAPS	8.45	3.0
TRIS	8.23[b]	55
TES	7.56	1.2
BES	7.26	0.53
BISTRIS	6.85	0.022
MES	6.36	0.82
HPO_4^{2-}	6.13[b]	24

[a] Taken as the pH of a half-neutralized solution. [b] Determined by potentiometric titration.

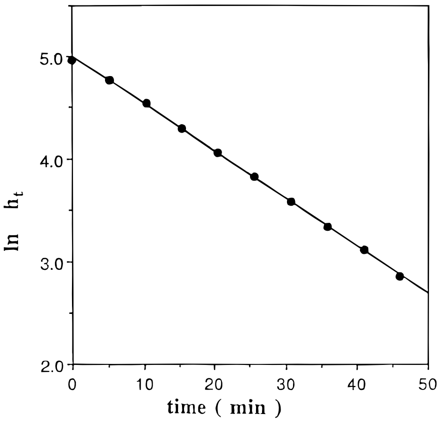

Figure 5. First-order plot of loss of ^{17}O label from Cr(VI) (0.0272 M, 40% ^{17}O enriched) into H_2O at pH 7.39 (TES buffer, 0.10 M) and 25 °C (I = 1.0, $NaClO_4$).

C. ^{17}O Exchange. Two mechanisms for oxygen exchange are likely. Exchange can either be direct via routes such as those given in Scheme 1 (and analogous paths involving $Cr_2O_7^{2-}$), or it can occur via the dimerization process expressed by eq 1 (a combination of the two is also possible). The two mechanisms give rates of exchange having different Cr(VI) and pH dependencies. In this section we use the observed rate constants for dimerization (α and β, part B**)** to calculate the rates of O exchange via this pathway (ν_3, eq 26) and compare these with observed rates of ^{17}O exchange. We then discuss the mechanism.

C1. Rates at Low Cr(VI) Concentrations (<0.15 M), I = 1.0 M. When ^{17}O-enriched Na_2CrO_4 is dissolved in normal water, decay of the chromate signal coincides with an increase in the height of the H_2O signal. For 40% ^{17}O enrichments and [Cr(VI)] > 0.15 M, the former peak does not decay to zero due to significant ^{17}O concentrations at equilibrium, but at lower [Cr(VI)], it disappears into the background after approximately three half-lives. Figure 5 gives a plot of ln(h_t) versus time for exchange at pH 7.39 and [Cr(VI)] = 0.0272 M with the linear

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(52) Brasch, N. E.; Buckingham, D. A.; Clark, C. R. *Inorg. Chem.* **1994**, *33*, 2683.

(53) Brasch, N. E.; Buckingham, D. A.; Clark, C. R. *Aust. J. Chem.* **1994**, *47*, 2283.

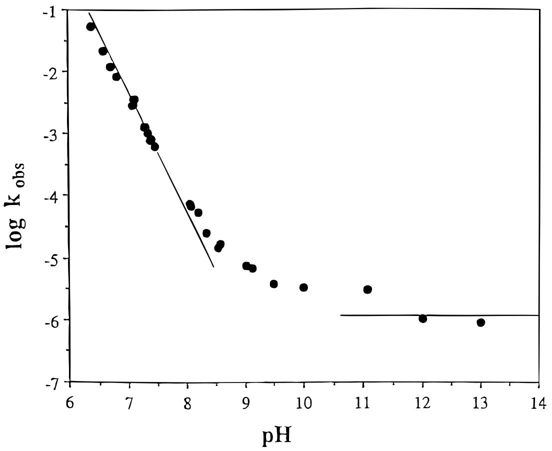
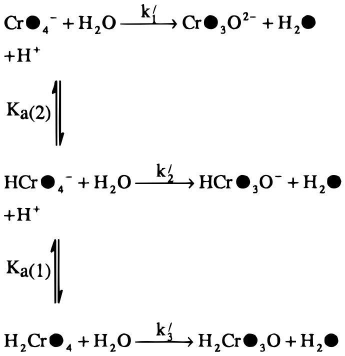


Figure 6. Plot of log k_{obs} versus pH for loss of ^{17}O label from Cr(VI) (0.01−0.152 M, 40% ^{17}O enriched) into H_2O, 25 °C, I = 1.0 M ($NaClO_4$).

Scheme 1



correspondence showing that the reaction is first-order, $k_{obs} = 7.75 \times 10^{-4}\ s^{-1}$. Similar first-order plots were obtained for all exchanges irrespective of Cr(VI) concentration, buffer condition, and pH.

First-order rate data (k_{obs}) are listed in Table 11. Before considering their pH dependence it is important to mention that k_{obs} is independent of Cr(VI) concentration and buffer concentration. This, observation is important when making decisions concerning the mechanism. The pH dependence is plotted in Figure 6. Two lines are drawn to show the two main dependencies. The slope of 2.0 suggests that for pH < 8 a close to second-order dependence on $[H^+]$ holds. The horizontal line for data above pH 10 suggests that k_{obs} is pH independent under such conditions. Closer examination however shows that the data do not agree exactly with these slopes, especially below pH 7, where a less than second-order dependence is seen, and in the pH region 8−10, where k_{obs} is larger than expected. The former suggests that protonation to form $HCrO_4^-$ ($pK_a = 5.80$) is reducing the pH dependence below pH 7, and the latter suggests that there is a term first-order in $[H^+]$ which contributes in the pH 8−10 region.

Table 11 also gives α and β values for the various buffer and pH conditions employed in the O-exchange measurements (columns 4 and 5), and rates of exchange calculated assuming the dimerization mechanism is responsible (v_3, column 6). Comparison with k_{obs} (column 7) shows no agreement. This is especially significant for the low-pH data where v_3 is some 100 times smaller than k_{obs}. Furthermore, v_3 shows a buffer dependence whereas k_{obs} does not. Dimerization (v_3) must contribute to O exchange, but clearly is not a major pathway.

Following Okumura,[9] we attribute the major pathways for exchange to direct exchange into CrO_4^{2-} (k_1'), $HCrO_4^-$ (k_2'), and H_2CrO_4 (k_3'). Scheme 1 leads to the expression

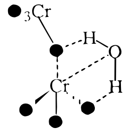
$$k_{calc} = (k_1'K_{a(2)} + k_2'a_{H^+} + k_3'a^2_{H^+}/K_{a(1)})/(K_{a(2)} + a_{H^+}) \quad (37)$$

where $K_{a(1)}$ represents the acidity constant for H_2CrO_4 and $K_{a(2)}$ that for $HCrO_4^-$ (5.80). The final column of Table 11 gives the least-squares fit to the observed data resulting in k_1', k_2', and $k_3'/K_{a(1)}$ values of $1.0 \times 10^{-6}\ s^{-1}$, $1.05 \times 10^{-2}\ s^{-1}$, and $5.8 \times 10^5\ M^{-1}\ s^{-1}$, respectively, under the I = 1.0 M ($NaClO_4$), 25 °C, condition. Assuming that $K_{a(1)}$ = 4.1 M,[54] k_3' takes on the value $2.4 \times 10^6\ s^{-1}$. Clearly the effects of protonating CrO_4^{2-} are appreciable.

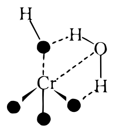
C2. Rates at Concentrations of Cr(VI) up to 2.0 M, I = 6.0 M. Like Okumura[9] we also found that for pH values < 7.5 the rate of O exchange increases with Cr(VI) concentration above ~0.1 M. Under this condition significant amounts of $Cr_2O_7^{2-}$ are present. Figure 7 gives one such plot at [Cr(VI)] = 2.0 M (pH 7.26), where $t_{1/2}$ for exchange is 2.4 min. This is to be compared with $t_{1/2}$ ~ 10.5 min for [Cr(VI)] = 0.02 M at the same pH. Table 12 gives k_{obs} values (column 6) for the concentration range 2.0−0.02 M. Na_2SO_4 was used as the supporting electrolyte to keep both the ionic strength (I = 6.0 M) and $[Na^+]$ constant.[55] Difficulties were experienced in measuring pH for these solutions (due to subsequent crystallization of Na_2SO_4 in the NMR tube), so that while good reproducibility in rate was achieved for a particular solution $[H^+]$ was less certain. Using measured K_a and K_d values in 6 M $NaClO_4$ (Table 3), rates for the dimerization mechanism (v_3, eq 26) were calculated, and these are listed in column 5. Once again it can be seen that dimerization does not account for the increase in exchange rate; it contributes only a maximum of ~10% under the 2.0 M condition. Direct exchange into $Cr_2O_7^{2-}$ is therefore suggested,[56] Scheme 2, and this leads to the expression

$$k_{calc} = (k_3'a_{H^+}{}^2/K_{a(1)} + k_4'K_d[HCrO_4^-]a_{H^+})/(K_{a(2)} + a_{H^+}(1 + K_d[HCrO_4^-]) \quad (38)$$

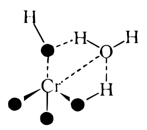
with exchange at lower pH being almost entirely via the k_3' pathway (for H_2CrO_4, cf. Scheme 1) and via the unassisted exchange into $Cr_2O_7^{2-}$ (k_4'). The final column of Table 12 gives the least-square fit to the observed data, resulting in $k_3'/K_{a(1)}$ and k_4' values of $1.2 \times 10^6\ M^{-1}\ s^{-1}$ and $3.8 \times 10^{-2}\ s^{-1}$, respectively. The former is within a factor of 2 of the value in 1.0 M $NaClO_4$. The latter corresponds to spontaneous exchange into $Cr_2O_7^{2-}$, and its value is similar to that for unassisted hydrolysis ($k_{-1} = 0.030\ s^{-1}$). Thus cleavage of the terminal and bridging Cr−O bonds appear to be equally likely. This is represented by the concerted transition state **1** with bonds to the bridging and terminal O atoms undergoing cleavage.



1



2



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[54] Tong, J. Y.; Johnson, R. L. *Inorg. Chem.* **1966**, *5*, 1902.

[55] Other extensive data (ref 37) showed that the rate was affected by specific cations rather than by the ionic strength.

[56] This is presumably the explanation of Okumura's data (ref 9) also, which was attributed entirely to dimerization.

[57] Grace, M. R.; Tregloan, P. A. *Inorg. Chem.* **1992**, *31*, 4524.

[58] Muirhead, K. A.; Haight, G. P.; Beattie, J. *J. Am. Chem. Soc.* **1972**, *94*, 3006.

Table 11. Observed and Calculated Rate Constants for ^{17}O Exchange at Low Cr(VI) Concentrations (<0.152 M) (I = 1.0 M (NaClO$_4$), 25 °C)

pH	10^2[Cr(VI)]/M	[B]$_T$/M	α^a/M^{-1} s^{-1}	$10^2\beta^b$/s^{-1}	$\nu_3{}^c$/s^{-1}	k_{obs}/s^{-1}	$k_{calc}{}^d$/s^{-1}
6.38	2.7	0.20 MES	2.8	3.5	4.9×10^{-4}	5.3×10^{-2}	5.2×10^{-2}
6.59	2.7	0.20 BISTRIS	2.6	3.3	2.2×10^{-4}	2.2×10^{-2}	2.2×10^{-2}
6.71	8.5	0.20 BISTRIS	2.6	3.3	4.0×10^{-4}	1.2×10^{-2}	1.3×10^{-2}
6.82	15.2	0.20 BISTRIS	2.6	3.3	4.4×10^{-4}	8.55×10^{-3}	8.5×10^{-3}
7.08	1.5	0.20 BES	2.6	3.3	1.7×10^{-5}	2.9×10^{-3}	2.9×10^{-3}
7.09	1.6	0.20 BES	2.6	3.3	1.7×10^{-3}	3.0×10^{-3}	2.8×10^{-3}
7.10	2.7	0.20 BES	2.6	3.3	2.8×10^{-5}	3.55×10^{-3}	2.7×10^{-3}
7.11	2.6	0.20 BES	2.6	3.3	2.6×10^{-5}	3.6×10^{-3}	2.6×10^{-3}
7.28	1.3	0.20 TES	2.6	3.3	6.1×10^{-6}	1.3×10^{-3}	1.3×10^{-3}
7.29	2.8	0.20 TES	2.6	3.3	1.25×10^{-5}	1.3×10^{-3}	1.2×10^{-3}
7.33	9.0	0.20 TES	2.6	3.3	3.3×10^{-5}	1.0×10^{-3}	1.1×10^{-3}
7.39	2.7	0.10 TES	2.6	3.3	7.75×10^{-6}	7.75×10^{-4}	8.5×10^{-4}
7.40	2.7	0.20 TES	2.6	3.3	7.4×10^{-6}	7.5×10^{-4}	8.1×10^{-4}
7.41	2.7		2.5	3.1	6.8×10^{-6}	8.1×10^{-4}	7.8×10^{-4}
7.47	5.4	0.20 TES	2.6	3.3	1.1×10^{-5}	6.2×10^{-4}	6.3×10^{-4}
8.06	1.0	0.20 TAPS	2.8	3.5	1.5×10^{-7}	7.4×10^{-5}	8.4×10^{-5}
8.07	2.7	0.20 TAPS	2.8	3.5	3.8×10^{-7}	7.0×10^{-5}	8.2×10^{-5}
8.19	2.6	0.133 TES	2.8	3.5	2.1×10^{-7}	5.3×10^{-5}	5.85×10^{-5}
8.33	1.1	0.200 TAPS	3.0	3.8	5.0×10^{-8}	2.5×10^{-5}	4.0×10^{-5}
8.34	1.1	0.20 TAPS	3.2	4.0	2.0×10^{-8}	1.5×10^{-5}	2.3×10^{-5}
8.57	2.5	0.267 TAPS	3.3	4.1	4.1×10^{-8}	1.7×10^{-5}	2.1×10^{-5}
9.03	3.0	0.20 CHES	5.6	7.0	1.0×10^{-8}	7.7×10^{-6}	7.4×10^{-6}
9.12	1.2	0.40 TAPS	4.8	6.0	2.3×10^{-9}	6.9×10^{-6}	6.2×10^{-6}
9.50	2.6	0.20 CHES	9.9	12.4	1.8×10^{-9}	3.8×10^{-6}	3.1×10^{-6}
9.99	2.6	0.20 CHES	19.1	23.9	3.6×10^{-10}	3.3×10^{-6}	1.7×10^{-6}
11.08	2.6	0.20 CAPS	136	1.7×10^{2}	1.7×10^{-11}	3.0×10^{-6}	1.05×10^{-6}
12.00	2.8		1.01×10^{3}	1.26×10^{3}	2.0×10^{-12}	1.0×10^{-6}	1.0×10^{-6}
13.00	2.7		1.01×10^{4}	1.26×10^{4}	1.9×10^{-13}	9.1×10^{-7}	1.0×10^{-6}

[a] $\alpha = k_1 + k_2a_{H^+} + k_3a_{OH^-} + k_4$[B] using $k_1 = 2.5$ M^{-1} s^{-1}, $k_2 = 4.0 \times 10^5$ M^{-2} s^{-1}, $k_3 = 1.01 \times 10^5$ M^{-2} s^{-1}, and $k_4 = 80k_{-4}$ (k_{-4}, Table 10). [b] $\beta = k_{-1} + k_{-2}a_{H^+} + k_{-3}a_{OH^-} + k_{-4}$[B] using $k_{-1} = 0.031$ s^{-1}, $k_{-2} = 5.0 \times 10^3$ M^{-1} s^{-1}; $k_{-3} = 1.26 \times 10^3$ M^{-1} s^{-1}, and k_{-4} values, Table 10. [c] ν_3 calculated using eq 26 and listed α and β values. [d] Calculated using eq 37 and $k_1' = 1.0 \times 10^{-6}$ s^{-1}, $k_2' = 1.05 \times 10^{-2}$ s^{-1}, $k_3'/K_{a(1)} = 5.8 \times 10^5$ M^{-1} s^{-1}, and $K_{a(2)} = 1.6 \times 10^{-6}$ M.

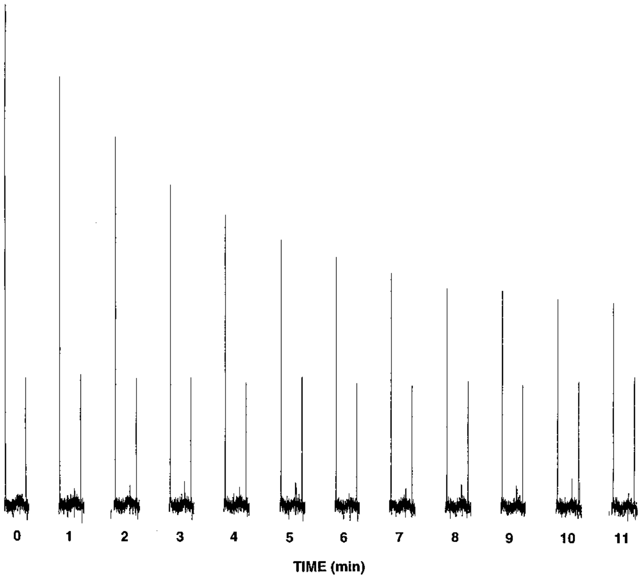
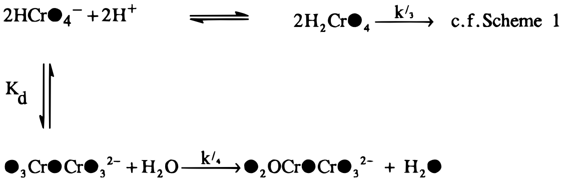


Figure 7. ^{17}O NMR spectra showing progressive loss of label from 2.0 M Cr(VI) (16 mg of Na$_2$CrO$_4$, 40% ^{17}O enriched) to H$_2$O at pH 7.26 and 25 °C, I = 6.0 M (referenced to external MoO$_4{}^{2-}$ at 529 ppm, signal at right).

Likewise, cyclic transition states **2** and **3** are used for concerted exchange into HCrO$_4{}^-$ and H$_2$CrO$_4$ with H-bonding to the solvent being an important feature. Such addition–elimination processes are supported by a recent study on Cr$_2$O$_7{}^{2-}$ in which rate-limiting addition of HPO$_4{}^{2-}$ has been interpreted in terms of formation of a transient five- (or six-) coordinate Cr(VI) intermediate.[53]

Scheme 2



C3. Comparisons with Other Substitutions on Cr(VI). This study substantiates Okumura's earlier ^{18}O study[9] that solvent O exchange into monomeric CrO$_4{}^{2-}$, HCrO$_4{}^-$, and H$_2$CrO$_4$ occurs directly. Our rate constants are 1.0×10^{-6} s^{-1}, 1.05×10^{-2}, and 2.4×10^6 s^{-1}, respectively, for the three monomeric species. By converting these to a per O basis and expressing them as second-order rate constants (c.f Scheme 1), these take on values of 7.2×10^{-8}, 7.6×10^{-4}, and 1.7×10^5 M^{-1} s^{-1}. Likewise, solvent exchange into Cr$_2$O$_7{}^{2-}$ on a per O basis has a rate constant of 4×10^{-3} M^{-1} s^{-1}. Table 13 compares these values with other known nucleophilic substitutions at Cr(VI). Two general observations can be made: (1) H$_2$O, and CrO$_4{}^{2-}$ in the dimerization reaction, are poor nucleophiles compared to the others and (2) the charge on the nucleophile is important. Thus HCrO$_4{}^-$ is better than CrO$_4{}^{2-}$, but so too is (NH$_3$)$_5$CoOH^{2+} compared to (NH$_3$)$_5$CoOH$_2{}^{3+}$; H$_2$PO$_4{}^-$ is the reactive phosphate species with HCrO$_4{}^-$, whereas HPO$_4{}^{2-}$ reacts more rapidly with Cr$_2$O$_7{}^{2-}$. Such features are likely to be important in biological oxidation processes using Cr(VI), and we will now be turning our attention to a study of these.

Experimental Section

Apparatus and Reagents. Spectrophotometric measurements were carried out using Cary 219 and Durrum D110 stopped-flow spectrophotometers. ^{17}O NMR spectra were recorded using a Varian VXRS 300 MHz spectrometer, operating at 40.662 MHz with a Varian coaxial 10 mm thermostated (25 °C) probe. Samples were contained in 10 mm NMR tubes with an external 5 mm aqueous ^{17}O-enriched Na$_2$-

Table 12. Observed and Calculated Rate Constants for ^{17}O Exchange at Variable Cr(VI) Concentrations ($I = 6.0$ M (Na_2SO_4), 25 °C)

[Cr(VI)]/M	pH	$10^4[Cr_2O_7^{2-}]$/M	$10^4[HCrO_4^-]$/M	$10^6\nu_3{}^a/s^{-1}$	$10^4k_{obs}/s^{-1}$	$10^4(k_{obs} - \nu_3)/s^{-1}$	$10^4k^b{}_{calc}/s^{-1}$
2.0	7.26	1190	297	521	48	43	29
2.0	7.59	321	154	125	11	9.85	7.3
2.0	7.79	134	99.5	52	4.4	3.9	3.0
1.0	7.15	510	194	400	36.5	32.5	34
1.0	7.16	492	191	400	36	32	32
0.50	7.15	141	102	220	30	28	27
0.20	7.27	14.3	32.5	86	15	14	12.5
0.10	7.26	3.8	16.6	29.4	12	11.5	12.4
0.060	7.27	1.31	9.96	17.0	10.5	10.3	11.4
0.040	7.30	0.51	6.15	9.90	9.1	9.0	9.8
0.020	7.32	0.117	2.94	4.53	9.1	9.05	8.8

[a] Calculated using eq 26 with $\alpha = 4.18$ M^{-1} s^{-1} and $\beta = 0.031$ s^{-1}. [b] Calculated using eq 38 with $k_3'/K_{a(1)} = 1.2 \times 10^6$ M^{-1} s^{-1}, $K_{a(2)} = 3.2 \times 10^{-6}$ M, $K_d = 132$ M^{-1}, and $k_4 = 3.8 \times 10^{-2}$ s^{-1}.

Table 13. Second-Order Rate Constants for Substitution into $HCrO_4^-$ and $Cr_2O_7^{2-}$ ($I = 1.0$ M, 25 °C)

$HCrO_4^- + Y \rightarrow$			$Cr_2O_7^{2-} + Y \rightarrow$		
Y	k/M^{-1} s^{-1}	ref	Y	k/M^{-1} s^{-1}	ref
H_2O	8×10^{-4}	*a*	H_2O	4×10^{-3}	*a*
CrO_4^{2-}	5.3×10^{-4}	*a*	HPO_4^{2-}	24	53
$H_2PO_4^-$	1.05	53	TRIS	55	52
$HCrO_4^-$	2.4	*a*			
$(NH_3)_5CoOH_2^{3+}$	2.5	57			
$(NH_3)_5CoOH^{2+}$	242	57			
$HS_2O_3^-$	2×10^4	58			

[a] This work.

MoO_4/D_2O reference and lock ($\delta^{17}O = 529$ ppm) or external 5 mm D_2O/DCl lock. The former reference was prepared by adding a few drops of ^{17}O-enriched H_2O to a saturated solution of Na_2MoO_4 in D_2O (0.7 cm^3). Spectra were obtained using the standard Varian 1D pulse sequence with an acquisition time of 0.15 s, a delay of 0.05 s, a 90° pulse angle, and a spectral window of 10^5 Hz. The pulse repetition time was sufficient to allow complete relaxation of the ^{17}O nuclei.

Solution pH was measured using a PHM 62 standard pH meter equipped with either G2020B/K4040 electrodes or an Ingold 6030-02 pH electrode designed to fit inside the NMR tube. Both electrodes were standardized using 0.025 M Na_2HPO_4/0.025 M KH_2PO_4 (pH (25 °C) = 6.86) and either borax buffer (0.01 M, pH (25 °C) = 9.18) or potassium hydrogen phthalate (0.05 M, pH (25 °C) = 4.01). Measurements on alkaline solutions were carried out under a nitrogen atmosphere.

^{17}O-labeled Na_2CrO_4 was prepared by dissolving ~1 g of Na_2CrO_4 (AR, recrystallized, dried) in 2 cm^3 of 40 atom % $H_2{}^{17}O$ (Yeda; this material also contained ~35% ^{18}O), with equilibration for 2 weeks at ~40 °C. Enriched water was subsequently recovered on the vacuum line.

Acidity (K_a) and Equilibrium (K_d) Constants. Spectrophotometric Titration. An 8.33×10^{-3} M solution of Na_2CrO_4 was made up in 1.0, 3.0, and 6.0 M $NaClO_4$, adjusted to pH 2.5, filtered, and diluted to give 2.08×10^{-5} M solutions. The pH was then successively altered over the range 2.5−10.0 by microliter additions of 1 M NaOH, the pH recorded (25 °C), and the absorbance at 370 nm measured.

Potentiometric Titration. A 40.00 cm^3 volume of 0.0100 M Na_2CrO_4 ($I = 1.0$ M, $NaClO_4$) was titrated with 0.10 and 0.20 cm^3 aliquots of 0.203 M $HClO_4$ ($I = 1.0$ M, $NaClO_4$) at 25 °C. The pH was recorded after each addition.

^{17}O NMR Titration. (a) 11.71 mg of Na_2CrO_4 and 0.404 g of $NaCF_3SO_3$ were dissolved in ~40% ^{17}O-labeled H_2O (total volume 2.7 cm^3, $[Cr_T] = 0.025$ M, $[CF_3SO_3^-] = 0.87$ M). This was transferred to the NMR tube and titrated stepwise with microliter additions of ~5 M CF_3SO_3H. After each addition the pH was measured and the ^{17}O spectrum recorded. The pH was remeasured before the next addition of CF_3SO_3H. (b) 76 mg of Na_2CrO_4 and 0.21 g of $NaCF_3SO_3$ were dissolved in 35% ^{17}O-labeled H_2O (total volume 2.6 cm^3, $[Cr_T] = 0.18$ M, $[CF_3SO_3^-] = 0.46$ M) and treated as above. (c) 0.135 g of Na_2CrO_4 (0.32M) was dissolved in 5% ^{17}O-labeled H_2O to give a total volume of 2.6 cm^3 ($[Cr_T] = 0.32$ M) and treated as above.

For the measurement of K_d, Na_2CrO_4 (81 mg) and 0.172 g of $NaCF_3SO_3$ or 0.546 g of Na_2SO_4 were dissolved in 2.5 cm^3 of 5% ^{17}O-labeled H_2O ($I = 1.0$ M, 6.0 M, respectively) and the pH adjusted to 6.52, 6.10, 6.04, 5.74, or 5.83 using microliter additions of 2 M CF_3SO_3H.

Spectrophotometric Rate Measurements (α and β). Rate data for the uncatalyzed reaction were obtained by mixing Na_2CrO_4 solutions (0.0333−0.133 M, $I = 1.0$ M, $NaClO_4$) with equal volumes of $Na_2Cr_2O_7$ solutions (0.0167−0.0667 M, $I = 1.0$ M, $NaClO_4$) containing indicator (2.0×10^{-5} M, phenol red, chlorophenol red, or bromothymol blue) at 25 °C in the Durrum. The resulting change in absorbance (557, 575, or 620 nm, respectively) was monitored as a function of time. Absorbance versus time data in acidic solution were obtained in a similar manner by mixing a 1.66×10^{-4} to 6.66×10^{-3} M Na_2CrO_4 solution ($I = 1.0$ M, $NaClO_4$) with 0.005−0.020 M $HClO_4$ ($I = 1.0$ M, $NaClO_4$) at 385, 400, or 416 nm. Data in alkaline solutions were recorded after mixing $Na_2Cr_2O_7$ solutions (1.17×10^{-3} M, $I = 1.0$ M, $NaClO_4$) and NaOH solutions (0.033−0.100 M, $I = 1.0$ M, $NaClO_4$) at 450 nm, while data in the presence of buffers were obtained after mixing $Na_2Cr_2O_7$ solutions (1.00×10^{-3} to 4.167×10^{-3} M, $I = 1.0$ M, $NaClO_4$) with buffers (0.05−0.20 M, $I = 1.0$ M, $NaClO_4$) at 450−480 nm. All data were collected using an OLIS 3820 stopped-flow data collection system in conjunction with a Northstar Horizon computer interfaced to the Durrum spectrophotometer. Data were treated using the OLIS nonlinear least-squares fitting routine Versatile Data Fit. Approach to equilibrium was first-order in all cases. For each experiment a separate solution was made up by mixing equal volumes of the two reagents and the pH recorded.

Oxygen Exchange Measurements. Solutions for exchange reactions with half-lives greater than ~55 s were prepared by dissolving ^{17}O-enriched Na_2CrO_4 (4.0−11.0 mg), normal unenriched Na_2CrO_4 (0−0.79 g), and $NaClO_4$ or Na_2SO_4 (if necessary) in 2.5 cm^3 of H_2O, or buffer solutions (0.133−0.40 M; MES, BISTRIS, BES, TES, TAPS, CHES, CAPS; $I = 1.0$ M, $NaClO_4$) or NaOH (1.00×10^{-2} or 1.00×10^{-1} M, $I = 1.0$ M, $NaClO_4$). The pH was adjusted (concentrated $HClO_4$) and the solution transferred to the 10 mm diameter NMR tube. Thermal equilibration in the spectrometer was carried out for about 2 min prior to data collection. More rapid exchange required that the separate components were thermostated (25 °C) before mixing. Reactions for which the half-lives were less than 12 h remained in the NMR probe during data collection. For reactions with longer half-lives the solutions were capped and stored in a constant-temperature bath (25 °C) between data collections. For rapidly exchanging conditions ($t_{1/2} < 55$ s) a quenching procedure was used. Na_2CrO_4 solutions containing NaOH (0.10 M, $I = 1.0$ M, $NaClO_4$) were mixed with an appropriate buffer solution (BISTRIS, MES), and the reaction quenched at various times by adding an equal volume of NaOH solution (0.20 M, $I = 1.0$ M, $NaClO_4$). NMR spectra were recorded shortly afterwards.

Difficulties were initially experienced in obtaining reproducible exchange data for pH > 9. Duplicate measurements differed by as much as 400%. Previous investigators have considered the possibility of glass catalysis,[59] and we found that the problem disappeared when Teflon containers were used. Thus, all CHES, CAPS, and NaOH

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(59) Winter, E. R. S.; Carlton, M.; Briscoe, H. V. A. *J. Chem. Soc.* **1940**, 131.

solutions were made up and immediately transferred to capped Teflon containers for storage. ^{17}O NMR exchange data were obtained using Teflon-lined NMR tubes under this condition.

It was not found necessary to use integrated peak areas as a measure of the ^{17}O concentration as the peak shape was constant for each experiment. When integrated areas were used these gave the same results as those obtained using peak heights. For slow exchanges (i.e., $t_{1/2} > 10$ h), an external ^{17}O reference of Na_2MoO_4 (529 ppm) was used. In such cases relative peak heights were used; i.e., $\ln(h_t/h_r - h_\infty/h_r)$ versus time plots, where h_r represents the height of the $Mo^{17}O_4^{2-}$ signal.

Errors. pH measurements were estimated to have an error of ±0.02−0.04 units (depending on electrode system) which corresponds to an error of 5−10% in a_{H^+}. First-order rate constants (stopped-flow) are estimated to have an error of 3%, while derived second-order rate constants ($k = k_{obs}/[X]$) are estimated to have an error of 5−10%. First-order rate constants obtained by ^{17}O NMR spectroscopy are estimated to have an error of 5−10% depending on the signal to noise ratio and line width. Integrated areas are estimated to have a maximum error of 5%.

Supporting Information Available: Tables 4 and 6−9 containing ^{17}O chemical shift data for pK_a ($HCrO_4^-$) and K_d determinations and rate constants for the acid, neutral, and alkaline equilibration or hydrolysis of $Cr_2O_7^{2-}$, respectively (5 pages). See any current masthead page for ordering and Internet access instructions.

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