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Notes

Hydrolysis of $Cr_2O_7^{2-}$. Nucleophilic Catalysis by TRIS and Rate Laws for the Formation and Decay of a (TRIS)CrO_3 Intermediate

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Introduction

As part of a ^{17}O study of oxygen exchange into $HCrO_4^-$ and $Cr_2O_7^{2-}$ in aqueous solution, we have had cause to re-examine the buffer-catalyzed hydrolysis of $Cr_2O_7^{2-}$, eq 1. The classic work in

$$B + Cr_2O_7^{2-} + H_2O \rightarrow B + 2HCrO_4^- \rightleftharpoons 2CrO_4^{2-} + 2H^+ \quad (1)$$

this area by Perlmutter-Hayman and associates in the 1960's[1,2] established both general acid (HOAc and chloroacetic acid) and base (some 36 oxygen and nitrogen bases were examined) pathways in addition to H^+- and OH-catalyzed and spontaneous reactions, eq 2, but although Perlmutter-Hayman suggested a

$$k_{obs} = k_0 + k_H[H^+] + k_{OH}[OH^-] + k_{AH}[AH] + k_B[B] \quad (2)$$

direct nucleophilic role for B, eq 3, it was never proven. In other

$$Cr_2O_7^{2-} + B \xrightarrow[k_1,\text{slow}]{} BCrO_3 + CrO_4^{2-} \xrightarrow[k_2,\text{fast}]{H_2O} HCrO_4^- + B + H^+ \quad (3)$$

reports large negative entropies[3] and volumes[4] of activation have been used to support a nucleophilic role for NH_3 and 2,6-lutidine, and the reverse reaction of $HCrO_4^-$ with oxyanions to give $BCrO_3$ products is well established.[5-8] This suggests that such intermediates are thermodynamically quite stable. However, only for B = $S_2O_3^{2-}$ has a mechanism involving nucleophilic catalysis been established.[8]

In our experiments we have found the reaction of $Cr_2O_7^{2-}$ with TRIS to be spectrophotometrically biphasic, thus requiring the formation of an intermediate. TRIS is traditionally regarded as a nonnucleophilic buffer so that this observation is of particular interest. Furthermore no reduction of Cr(VI) was evident in the time scale of the hydrolysis. This report details the rate laws for the formation and decay of this intermediate.

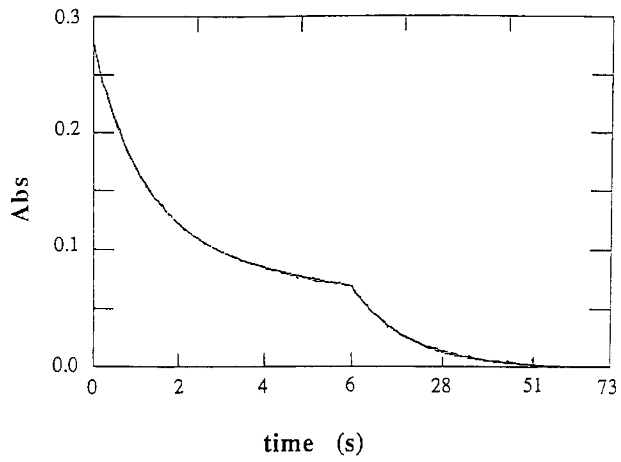

Figure 1. Variation of absorbance with time for the hydrolysis of $Cr_2O_7^{2-}$ in the presence of TRIS buffer ($[TRIS]_T$ = 0.050 M, $[Cr]_T$ = 4 × 10^{-3} M, λ = 450 nm, pH = 7.84, 25 °C). The data have been fitted to two consecutive first-order reactions with rate constants k_{fast} = 0.917 s^{-1} and k_{slow} = 0.080 s^{-1}, and the computed fit is superimposed on the experimental data. (Data were collected over two different time intervals: 0–6 and 6–73 s.)

Experimental Section

Rate data were collected using a Durrum D110 stopped-flow spectrophotometer interfaced to an OLIS 3820 data collection system and a Northstar Horizon computer. The OLIS nonlinear least-squares program Versatile Data Fit was used to minimize observed absorbance changes according to the expression $A_t - A_\infty = Me^{-k_{fast}t} + Ne^{-k_{slow}t}$ where k_{fast} and k_{slow} represent the first and second observed reactions and M and N are functions of the rate constants and the extinction coefficients of the reactants, intermediate, and products.[9] Rapid scan spectra were obtained using a Harrick rapid scan monochromator in association with the Durrum.

Equal volumes of a slightly acidified (pH 4.5) Na_2CrO_4 solution ((4.16–8.33) × 10^{-3} M, I = 1.0 M, $NaClO_4$) and TRIS buffer (0.100–0.500 M, I = 1.0 M, $NaClO_4$) were mixed in the Durrum spectrophotometer and the resulting absorbance decreases followed at 450 nm (25.0 °C). Under these conditions the reaction mixtures initially contained some 32–43% of $[Cr]_T$ as $Cr_2O_7^{2-}$ with the remainder being CrO_4^{2-} ($K_D = [Cr_2O_7^{2-}]/[HCrO_4^-]^2$ = 80 M^{-1}, $pK_a^c(HCrO_4^-)$ = 5.64).[10] Rapid-scan spectra had previously shown that 450 nm gave a significant absorbance change for the second reaction as well as a clear differentiation from the first. The pH (25 °C) of the recovered effluent was measured using a Radiometer PHM 62 pH meter equipped with G2020B/K4040 electrodes.

Acidity constants of buffer species (B/BH^+) are given as concentration constants, $K_a^c = [B][H^+]/[BH^+]$, with $[H^+]$ determined from pH measurements, pH = $-\log a_{H^+}$, $[H^+] = a_{H^+}/\gamma_\pm$, and $\gamma_\pm$ = 0.767 (25.0 °C, I = 1.0 M, $NaClO_4$).

Results

Figure 1 gives a typical absorbance–time trace for the hydrolysis of $Cr_2O_7^{2-}$ in the presence of TRIS buffer. Two rate processes are evident, both involving absorbance decreases. It was not possible to find a wavelength which gave absorbance changes in opposite senses, but the difference in time scales makes analysis of the rates quite straightforward. Table 1 lists rate constants k_{fast} and k_{slow} at different TRIS concentrations. Under the pH conditions 7.55–8.96, and at the low Cr(VI) concentrations used

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Table 1. Rate Data for the Hydrolysis of $Cr_2O_7^{2-}$ in the Presence of TRIS Buffer (25 °C, I = 1.0 M, $NaClO_4$)

$[TRIS]_T$ (M)	pH	$10^8[H^+]$ (M)	$[TRIS]^a$ (M)	k_{fast}(obs) (s^{-1})	k_{slow}(obs) (s^{-1})	$k_{slow}(calc)^b$ (s^{-1})	$k_{slow}(calc)^c$ (s^{-1})
0.250	7.55	3.67	0.0440	2.50	0.200	0.221	0.228
0.100	7.68	2.7324	0.0224	1.27	0.112	0.106	0.114
0.050	7.84	1.88	0.0147	0.917	0.080	0.063	0.074
0.100	7.86	1.80	0.0304	1.64	0.142	0.128	0.137
0.100	7.90	1.64	0.0324	1.83	0.157	0.133	0.142
0.250	8.02	1.25	0.0967	5.70	0.350	0.358	0.357
0.100	8.20	0.823	0.0487	2.70	0.175	0.150	0.160
0.200	8.22	0.786	0.100	5.70	0.310	0.300	0.300
0.400	8.23	0.768	0.202	11.4	0.580	0.600	0.579
0.200	8.24	0.750	0.102	5.87	0.325	0.299	0.299
0.100	8.60	0.327	0.0706	3.70	0.133	0.124	0.139
0.100	8.64	0.299	0.0725	3.80	0.130	0.119	0.134
0.250	8.80	0.207	0.198	10.00	0.220	0.244	0.246
0.100	8.96	0.143	0.0846	4.77	0.100	0.077	0.099

[a] $[TRIS] = K_a^c[TRiS]_T/([H^+] + K_a^c)$; $K_a^c = 6.03 \times 10^{-9}$ M. [b] Best fit of data to eq 5, with $k_2 = 6.2$ M^{-1} s^{-1} and $K_a^c = 8.3 \times 10^{-9}$ M for $(TRIS)CrO_3$. [c] Best fit of data to eq 6, with $k_2 = 6.4$ M^{-1} s^{-1}, $k_2' = 3.5 \times 10^{-10}$ M^{-1} s^{-1}, and $K_a^c = 1.0 \times 10^{-8}$ M for $(TRIS)CrO_3$.

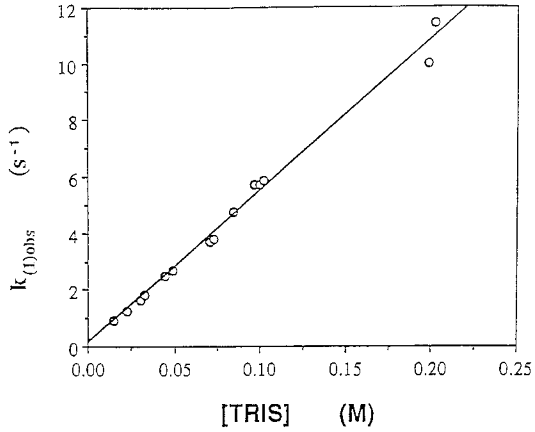


Figure 2. Plot of k_{fast} vs [TRIS] for reaction of $Cr_2O_7^{2-}$ at 25 °C and I = 1.0 M ($NaClO_4$).

((2.08–4.16) × 10^{-3} M), only hydrolysis of $Cr_2O_7^{2-}$ was important; reverse dimerization was negligible.[11] The final absorbance was shown to be identical to that of CrO_4^{2-} at the same pH in the absence of buffer, and the separate absorbance changes (ΔA_{fast}, ΔA_{slow}) were both shown to be independent of TRIS concentration. The latter fact means that the first reaction is not measurably reversible, and the former means that we are dealing only with (catalyzed) hydrolysis of $Cr_2O_7^{2-}$; i.e., no reduction of Cr(VI) to Cr(III) is involved in the time scale of the experiment. No reaction was observed when Cr(VI) and TRIS solutions initially at the same pH (i.e. ~8.0) were mixed; thus we are dealing with the reaction of $Cr_2O_7^{2-}$, and not of $HCrO_4^-/CrO_4^{2-}$, with TRIS.

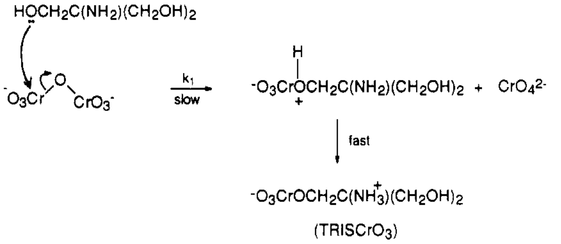
Discussion

Figure 2 gives a plot of k_{fast} vs [TRIS], where TRIS represents the basic form of the buffer. The linear correspondence establishes the rate law

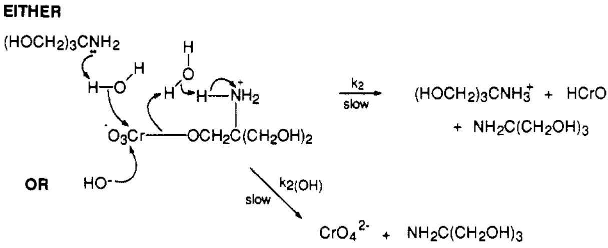
$$k_{fast} = k_1[TRIS] \qquad (4)$$

and the near-zero intercept confirms that spontaneous hydrolysis (k_0 = 0.03 s^{-1}) is insignificant. Also the fact that the data agree with eq 4 irrespective of pH confirms that OH^- catalysis (eq 2) is unimportant.[12] The rapidity of the first reaction compared to the second (at least a 10-fold difference in rate is involved) almost certainly means that the first observed reaction (Figure 1) corresponds to the first mechanistic process,[9] and hence we assign it to the addition of TRIS to $Cr_2O_7^{2-}$; k_1 = 55 M^{-1} s^{-1} at 25 °C and I = 1.0 M ($NaClO_4$).[13] Scheme 1 pictures this as a concerted addition–elimination process at Cr(VI) since we view five-coordinate Cr(VI) as a transition state rather than as a transient intermediate (proton transfer from O to N may also be synchronous). Perhaps the most unusual feature of this interpretation is that of TRIS functioning as an alcohol nucleophile rather than as an amine nucleophile, with the intermediate species being $^+H_3NC(CH_2OH)_2CH_2OCrO_3^-$ (designated $(TRIS)CrO_3$). This feature may be related to the oxidative properties of Cr(VI) toward alcohols in acidic solution[14,15] and suggests that direct attack by O nucleophiles at Cr(VI) is more facile than direct attack by amines.

Scheme 1



Scheme 2



The second reaction shows a more complex dependence on TRIS concentration and on pH. Consider the k_{slow} data at $[TRIS]_T$ = 0.100 M, Table 1. As the pH increases from 7.68 to 8.20, k_{slow} increases, but as the pH increases further (8.60, 8.64, 8.96), it now decreases. However at a fixed pH (e.g. 8.2) k_{slow} shows a linear increasing [TRIS]. This data fits reasonably well the rate law

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(11) Linge, H. G.; Jones, A. L. *Aust. J. Chem.* **1968**, *21*, 1445.

(12) Hydrolysis rate constants k_0 = 0.031 s^{-1}, $k_H = 4.0 \times 10^3$ M^{-1} s^{-1}, and $k_{OH} = 1.01 \times 10^3$ M^{-1} s^{-1} at 25.0 °C and I = 1.0 M ($NaClO_4$) have been confirmed by other work in this laboratory.

(13) A contribution to the rate constant k_1 (eq 4) from TRIS buffer catalyzed addition of solvent leading directly to hydrolyzed product (i.e. general base catalysis) cannot be ruled out by these results.

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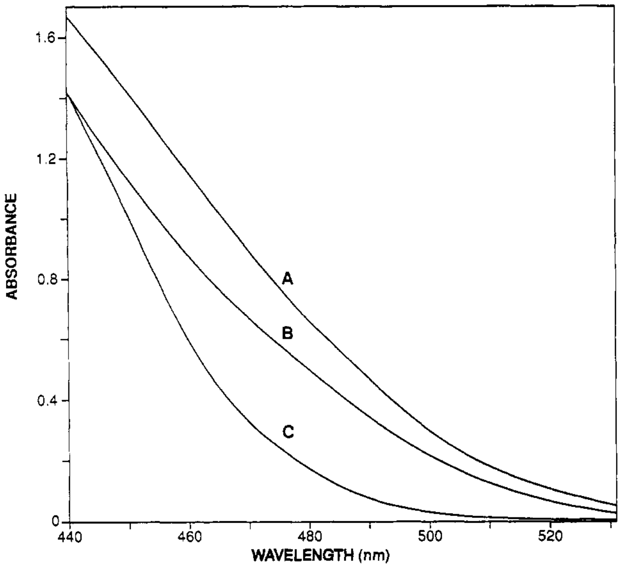

Figure 3. Spectra derived from rapid-scan measurements (440–540 nm, path length 2.0 cm) following ratio mixing (1:14.4) of 5.555×10^{-2} M Cr(VI) (pH 3.5) with 0.50 M TRIS buffer (I = 1.0 M ($NaClO_4$), $[Cr(VI)]_T = 3.607 \times 10^{-3}$ M, 25 °C, pH 8.8). Spectra correspond to the following: (A) 1.803×10^{-3} M $Cr_2O_7^{2-}$, calculated on the basis that the initial reaction mixture contains 1.291×10^{-3} M $Cr_2O_7^{2-}$ and 1.024×10^{-3} M CrO_4^{2-} (K_D = 80 M^{-1}; see text); (B) 3.607×10^{-3} M (TRIS)CrO_3, calculated on the basis that this species is fully formed 0.3 s ($10t_{1/2}$) after mixing and that the initial reaction has no general base component (cf. ref 13); (C) 3.607×10^{-3} M CrO_4^{2-}.

$$k_{\text{slow}} = \frac{k_2[\text{TRIS}][\text{H}^+]}{K_a^c + [\text{H}^+]} \qquad (5)$$

with $k_2 = 6.2\ M^{-1}\,s^{-1}$ and $K_a^c = 8.3 \times 10^{-9}$ M, where K_a^c represents the acid dissociation constant of the (TRIS)CrO_3 intermediate. Agreement is shown by the calculated rate constants given in the penultimate column of the table. A somewhat better fit (last column) is found by including a [TRIS]-independent pathway k_2', viz.

$$k_{\text{slow}} = \frac{k_2[\text{TRIS}][\text{H}^+] + k_2'}{K_a^c + [\text{H}^+]} \qquad (6)$$

Such a rate law is interpreted in terms of Scheme 2. The rate constant k_2 represents the general TRIS-base-catalyzed hydrolysis of (TRIS)CrO_3 and k_2' the solvolytic OH^- hydrolysis of the same species.[16] This interpretation gives $k_2 = 6.4\ M^{-1}\,s^{-1}$, $k_{2(OH)} = k_2'/K_w = 2.2 \times 10^4\ M^{-1}\,s^{-1}$, and $K_a^c = 1.0 \times 10^{-8}$ M. It suggests that TRIS is not as efficient a general base ($k_2 = 6.4\ M^{-1}\,s^{-1}$) as it is as a nucleophile ($k_1 = 55\ M^{-1}\,s^{-1}$), an observation supported by the fact that the OH^--catalyzed hydrolysis of (TRIS)CrO_3 is somewhat faster ($2.2 \times 10^4\ M^{-1}\,s^{-1}$) than the OH^--catalyzed hydrolysis of $Cr_2O_7^{2-}$ ($1.01 \times 10^3\ M^{-1}\,s^{-1}$). The acidity of the intermediate (TRIS)CrO_3 species ($pK_a^c = 8.0$) is similar to that of TRIS buffer itself ($pK_a^c = 8.12$), which is in keeping with the amine function not being involved in the first reaction. Spectra (440–540 nm) of $Cr_2O_7^{2-}$, CrO_4^{2-}, and the intermediate (TRIS)CrO_3 species are given in Figure 3.

Table 2. Second-Order Rate Constants for the Catalyzed Hydrolysis of $Cr_2O_7^{2-}$(25 °C, I = 1.0, $NaClO_4$)

catalyst[a]	pK^c_{buffer}[b]	k_B ($M^{-1}\,s^{-1}$)
CAPS	10.46	76
CHES	9.48	47
DABCO	9.18	4.35×10^3
TAPS	8.34	3.0
TRIS	8.12	55
TES	7.45	1.2
BES	7.15	0.53
BISTRIS	6.74	2.2×10^{-2}
MES	6.25	0.82

[a] CAPS, 3-(cyclohexylamino)-1-propanesulfonic acid; CHES, 2-(cyclohexylamino)ethanesulfonic acid; DABCO, 1,4-diazaobicyclo[2.2.2]-octane; TAPS, 3-[tris(hydroxymethyl)methylamino]-1-propanesulfonic acid; TRIS, tris(hydroxymethyl)aminomethane; TES, 2-[tris(hydroxymethyl)methylamino]-1-ethanesulfonic acid; BES, *N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid; BISTRIS, bis(2-hydroxyethyl)aminotris(hydroxymethyl)methane; MES, 4-morpholineethanesulfonic acid. [b] From pH measurements on half-neutralized solutions (0.20 M).

Apart from triethanolamine, which also gave clear indications of biphasic kinetics at 450 nm,[17] we were unable to find two-step spectrophotometric processes for other "nonnucleophilic" buffers, and the reactions followed a single exponential. Table 2 lists k_B values (eq 2). Of the buffers studied BISTRIS, TES, TAPS, and BES all contain–OH functionalities (BISTRIS has five), and we fully expected to see similar formation of (B)CrO_3 intermediates. It may be that in these cases decay of the intermediate is faster than its formation ($k_B = k_1$, eq 3). However, the bis tertiary amine DABCO is an especially effective catalyst ($k_B = 4.35 \times 10^3\ M^{-1}\,s^{-1}$) and is less likely to act as a nucleophile, so that an entirely general base catalyzed role[13] is possible for these bases.

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(16) Alternatively this could be interpreted as solvent (H_2O) assisted hydrolysis of the [(TRIS-H)CrO_3H]$^-$ conjugate base.

(17) Biphasic kinetics were clearly evident at 450 nm, but the optical density change for the second reaction was very small making its analytical separation from the first uncertain.