CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
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Kinetic Studies on the Hydrogen Chromate–Dichromate Reaction in Perchloric Acid Solutions[1a]

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Received June 16, 1970

The kinetics of the reaction $2HCrO_4^- = Cr_2O_7^{2-} + H_2O$ in perchloric acid solutions of pH 2–4 has been studied using the stopped-flow method. The reaction rate conforms to the rate expression $-d[Cr_2O_7^{2-}]/dt = k_1[Cr_2O_7^{2-}][H^+] - k_2[HCrO_4^-]^2 \cdot [H^+]$, with H^+ catalysis providing the only significant pathway in these acidic solutions. At 1.00 M ionic strength ($HClO_4$–$LiClO_4$ medium), the rate parameters are $k_1(25.0°) = (6.35 \pm 0.35) \times 10^3\ M^{-1}\ sec^{-1}$, $k_2(25.0°) = (6.22 \pm 0.34) \times 10^5\ M^{-2}\ sec^{-1}$, $\Delta H_1^{\ddagger} = 9.0 \pm 0.2$ kcal mol^{-1}, $\Delta S_1^{\ddagger} = -11.0 \pm 0.5$ cal mol^{-1} deg^{-1}, $\Delta H_2^{\ddagger} = 4.3 \pm 0.5$ kcal mol^{-1}, and $\Delta S_2^{\ddagger} = -17.7 \pm 1.5$ cal mol^{-1} deg^{-1}. The mechanism is discussed and the rate constants are compared to a related reaction, Cr(VI)–H_2O exchange.

Introduction

A number of kinetic studies[2–4] under various conditions have been published on reaction I, which is the

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \qquad (I)$$

principal equilibrium in weakly acidic Cr(VI) solutions.[5] The earlier kinetic work consists mainly of studies in basic solution or in acidic solutions under conditions where general acid catalysis was observed. We were concerned with evaluating the forward and reverse rates of reaction I under conditions similar to those generally used in studies on Cr(VI) oxidations—dilute acidic solutions containing perchlorate as the only anion.

The only work under such conditions appears to be that of Perlmutter-Hayman,[3b] who made a few rate measurements in $HClO_4$ solution as part of a larger study on the general-acid catalysis. The equilibrium constant, needed to resolve the kinetic data, is not known precisely under the conditions studied. Nevertheless, the conclusion that the rate constants in $HClO_4$ solution are directly proportional to $[H^+]$ was confirmed by the more extensive studies reported here.

The only important Cr(VI) species in 10^{-4}–10^{-2} F solutions of Cr(VI) of pH 2–4 are $HCrO_4^-$ and $Cr_2O_7^{2-}$; H_2CrO_4, $HCr_2O_7^-$, and CrO_4^{2-} remain negligible. The equilibrium constant for reaction I in $HClO_4$–$LiClO_4$ solutions of 1.00 M ionic strength is given by eq 1,[5] for which Hepler[6] reported the calorimetrically determined

$$K_d = [Cr_2O_7^{2-}]/[HCrO_4^-]^2 = 98\ M^{-1}\ (25.0°) \qquad (1)$$

value $\Delta H_d° = -4.7$ kcal (mol of $Cr_2O_7^{2-}$)$^{-1}$.

We have evaluated the forward and reverse rates of reaction I over a considerable range of Cr(VI) and H^+ concentrations and determined the activation parameters by studies at different temperatures. The reaction medium was a solution of $HClO_4$–$LiClO_4$ of ionic strength 1.00–1.02 M.

Experimental Section

Reagents.—Primary standard potassium dichromate was used for all the experiments. The high rate of the reaction limited the upper end of the H^+ variation to 0.01 M, so that experiments had to be carried out at low $[H^+]$, down to 10^{-4} M, to encompass a significant variation. Buffers could not be added, however, because their constituents catalyze the reaction.[3] Consequently the lithium perchlorate had to be exceptionally free of even a trace contamination by $HClO_4$ or Li_2CO_3. Some samples of $LiClO_4$ were obtained by neutralizing the carbonate with a slight excess of $HClO_4$ and were repeatedly recrystallized. In other cases the solution was obtained as above, CO_2 was expelled by boiling, and the remaining $HClO_4$ was neutralized by a small excess of LiOH. Lithium perchlorate was recrystallized from this solution under nitrogen to prevent contamination by atmospheric CO_2. A third preparation involved fuming lithium chloride solutions with perchloric acid, with four subsequent recrystallizations of the resulting $LiClO_4$ salt. Finally, commercial hydrated $LiClO_4$ (G. F. Smith) was recrystallized three times. These four preparations were then employed at a run with 5.00×10^{-4} M H^+ and 5.00×10^{-4} F Cr(VI), giving pseudo-first-order rate constants of 3.62 ± 0.08, 3.60 ± 0.05, 3.61 ± 0.10, and 3.66 ± 0.08 sec^{-1}, respectively.[7] With insufficient purification the rates were substantially different, being higher or lower depending on whether the contamination was an acidic or basic component.

Perchloric acid was prepared by diluting the reagent grade 72% acid. The hydrogen ion concentrations in the kinetic runs were taken as the formal concentration of perchloric acid in the analyzed stock solutions except at the lowest concentration, 1.0×10^{-4} F $HClO_4$, where a correction was made for the contribution from the acid dissociation reaction of $HCrO_4^-$ ($pK_a = 5.91$).[8]

Rate Measurements and Kinetic Data.—The reaction rate was studied by making a sudden twofold dilution of a Cr(VI) solution at constant $[H^+]$. The resulting equilibrium shift is accompanied by a decrease in absorbance because the molar absorptivity of $HCrO_4^-$ is considerably smaller than half that of $Cr_2O_7^{2-}$.[5a] The reaction occurred with half-times between 7.5

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[1] (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2775. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[2] R. N. J. Saal, *Recl. Trav. Chim. Pays-Bas*, **47**, 264 (1928); (b) V. K. La Mer and C. L. Read, *J. Amer. Chem. Soc.*, **52**, 3098 (1930); (c) G. Schwarzenbach and J. Meier, *J. Inorg. Nucl. Chem.*, **8**, 302 (1958).

[3] (a) A. Lifschitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, **65**, 2098 (1961); (b) B. Perlmutter-Hayman, *ibid.*, **69**, 1736 (1965); (c) B. Perlmutter-Hayman and Y. Weissman, *ibid.*, **71**, 1409 (1967); (f) B. Perlmutter-Hayman and M. A. Wolff, *ibid.*, **71**, 1416 (1967); (e) R. Baharad, B. Perlmutter-Hayman, and M. A. Wolff, *ibid.*, **73**, 4391 (1969).

[4] J. H. Swinehart and G. W. Castellan, *Inorg. Chem.*, **3**, 278 (1964).

[5] (a) J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **75**, 6180 (1953); (b) J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964).

[6] L. G. Hepler, *J. Amer. Chem. Soc.*, **80**, 6181 (1958).

[7] The last result and the fourth source of $LiClO_4$ were supplied by Mr. Robert J. Kinney, whose efforts we appreciate.

[8] Y. Sasaki, *Acta Chem. Scand.*, **16**, 719 (1962).

and 970 msec and was followed using a Durrum stopped-flow spectrophotometer at a wavelength between 390 and 510 nm.

The reaction followed first-order kinetics,[9] as expected[3,4] from the relatively small shift in equilibrium. The apparent first-order rate constants, k_{exptl}, evaluated from such plots proved to be independent of the wavelength used. Typically three determinations were made with given solutions, for which the average deviation of the individual values from the mean was generally ≤3%. Table I summarizes the values of k_{exptl} as a function of $[\text{HCrO}_4^-]_{\text{av}}$ and T.

TABLE I

KINETIC DATA FOR THE $HCrO_4^-$–$Cr_2O_7^{2-}$ REACTION

$[H^+]$, M x 10³	$[HCrO_4^-]$,[a] M x 10³	k_{exp}, s⁻¹ obsd[b]	k_{exp}, s⁻¹ calcd[c]
	T = 15.0°		
0.500	0.43	2.30±0.08	2.19
0.500	1.58	3.30±0.05	3.26
0.500	2.58	4.06±0.10	4.18
0.500	3.38	4.87±0.20	4.92
0.500	4.06	5.30±0.20	5.55
0.500	4.67	5.82±0.27	6.12
0.500	5.19	6.83±0.20	6.60
0.500	5.49	6.39±0.10	6.88
0.900	0.43	4.27±0.25	3.95
0.900	1.29	5.66±0.15	5.38
0.900	2.49	7.34±0.04	7.38
0.900	4.06	9.15±0.06	10.0
	T = 25.0°		
0.106	0.46	0.72±0.02	0.79
0.111	0.93	0.91±0.02	0.95
0.120	1.83	1.24±0.02	1.29
0.128	2.72	1.72±0.04	1.66
0.135	3.58	2.08±0.10	2.04
0.141	4.44	2.70±0.10	2.43
0.147	5.32	2.98±0.03	2.85
0.500	0.45	3.63±0.03	3.70
0.500	2.72	6.60±0.20	6.49
0.500	6.17	11.5±0.5	10.7
0.900	0.45	6.62±0.10	6.65
0.900	1.82	9.1 ±0.4	9.69
0.900	3.57	14.5±0.2	13.6
0.900	5.32	17.8±1.0	17.4
1.35	0.24	9.4 ±0.3	9.26
1.35	0.32	9.2 ±0.4	9.54
1.35	0.45	9.5 ±0.3	9.98
1.35	1.28	12.6±0.3	12.7
1.35	2.18	17.1±0.8	15.7
1.35	3.00	22.2±0.3	18.5
1.35	3.28	21.0±1.0	19.4
1.35	4.83	23.6±1.0	24.5
1.35	5.80	24.6±1.0	27.8
1.35	7.05	31.5±2.0	31.9
5.00	0.45	36.9±1.5	37.0
5.00	2.27	58.6±3.5	59.4
5.00	4.44	90.6±5.0	86.1
10.0	0.45	77.6±3.0	73.9
	T = 35.0°		
0.500	0.46	5.4 ±0.3	6.04
0.500	1.02	7.36±0.4	6.97
0.500	1.50	7.88±0.25	7.74
0.500	2.57	9.80±0.2	9.46
0.500	3.45	10.8±0.2	10.9
0.500	4.21	11.4±0.4	12.1
0.500	4.89	12.8±0.3	13.2
0.900	0.46	10.6±0.1	10.9
0.900	1.45	13.4±0.7	13.8
0.900	2.95	17.7±0.5	18.1
0.900	4.87	26.1±0.5	23.6

[a] The average $HCrO_4^-$ concentration during the run. [b] The uncertainty given is the average deviation from the mean in the repeat determinations, usually three per entry. [c] Calculated from the second column of activation parameters cited in Table IV.

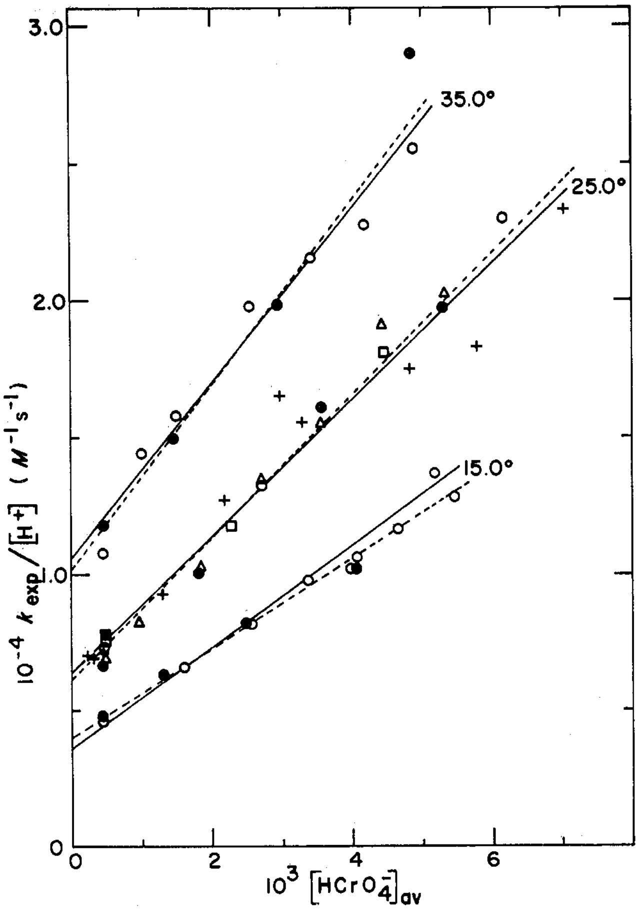

Figure 1.—A plot of $k_{\text{exptl}}/[\text{H}^+]$ *vs.* $[\text{HCrO}_4^-]_{\text{av}}$ in accord with eq 4 at each of three temperatures at various $[\text{H}^+]$: 1.0 × 10^{-4} *M*, triangles; 5.00 × 10^{-4} *M*, open circles; 9 × 10^{-4} *M*, filled circles; 1.35 × 10^{-3} *M* crosses; 5.00 × 10^{-3} *M*, open squares; 1.00 × 10^{-2} *M*, filled squares. The lines shown are least-squares fitted, the dashed line representing the cases where both parameters were free to refine to their "best" values, and the solid line the case where the quotient k_2/k_1 was constrained to the known value of K_d.

Results

Concentration Dependences.—The apparent rate constant k_{exptl} is expected[3b,4] to increase linearly with $[\text{HCrO}_4^-]_{\text{av}}$ according to the equation

$$k_{\text{exptl}} = k_1' + 4k_2'[\text{HCrO}_4^-]_{\text{av}} = k_1'\{1 + 4K_d[\text{HCrO}_4^-]_{\text{av}}\} \quad (2)$$

where the apparent rate constants at a given $[\text{H}^+]$ are defined by the rate law

$$d[\text{Cr}_2\text{O}_7^{2-}]/dt = k_2'[\text{HCrO}_4^-] - k_1'[\text{Cr}_2\text{O}_7^{2-}] \quad (3)$$

Plots of k_{exptl} *vs.* $[\text{HCrO}_4^-]_{\text{av}}$ are linear at a given $[\text{H}^+]$, from the slopes of which an equilibrium constant K_d = 98 ± 5 M^{-1} was found at 25.0°. The rate increase with $[\text{H}^+]$ noted here, as well as before,[3b] provides a more general method of correlating the rate data with the concentration variables. The work of Perlmutter-Hayman[3b] suggests k_1' is directly proportional to $[\text{H}^+]$, the acid-independent term[4] contributing negligibly at this pH. That being the case, the form of eq 1 and 2 would require that k_2' also be directly proportional to $[\text{H}^+]$. These concepts are incorporated in the relation

$$k_{\text{exptl}}/[\text{H}^+] = k_1 + 4k_2[\text{HCrO}_4^-]_{\text{av}} = k_1\{1 + 4K_d[\text{HCrO}_4^-]_{\text{av}}\} \quad (4)$$

Within the precision of the data, eq 4 correlates all the rate constants, as shown in Figure 1. A least-squares fit of the data at 25.0° gives k_1 = (6.08 ± 0.16) × 10^3 M^{-1} sec^{-1}, k_2 = (6.48 ± 0.21) × 10^5 M^{-2} sec^{-1}; the value of K_d derived from these numbers is 107 ± 6 M^{-1}. Alternatively, under the constraint that the rate constants must give precisely the known[5] K_d, the values are k_1 = (6.35 ± 0.35) × 10^3 M^{-1} sec^{-1} and k_2 = (6.22 ± 0.34) × 10^5 M^{-2} sec^{-1} at 25.0°.

Another method of considering the kinetic data as a function of the variables $[\text{HCrO}_4^-]_{\text{av}}$ and $[\text{H}^+]$, essentially equivalent to fixing K_d as above, provides a better basis for judging whether the proposed rate equation accounts for all the observations. According to eq 4, the value of k_1 is calculable from k_{exptl} given the value K_d

$$k_1 = \frac{k_{\text{exptl}}}{[\text{H}^+]\{1 + 4K_d[\text{HCrO}_4^-]_{\text{av}}\}} \quad (5)$$

The k_1 values thus calculated (Table II) do not vary systematically with $[\text{H}^+]$, confirming the conformance of the data to a single-term rate expression.

Temperature Dependence.—Kinetic experiments on reaction I were also carried out at 15.0 and 35.0°, with the results given in Table I and Figure 1. The least-

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[9] Very slight downward curvature was noted in runs having the highest Cr(VI) concentrations. Such runs have larger equilibrium shifts so that the approximation leading to the expectation of pseudo-first-order kinetics holds less precisely.

TABLE II

COMPUTED[a] VALUES OF k_1 FOR THE $HCrO_4^-$–$Cr_2O_7^{2-}$ REACTION

	$10^{-3}k_1$, M^{-1} sec^{-1}		
$10^3[H^+]$, M	15.0° (K_d = 129 M^{-1})	25.0° (K_d = 98 M^{-1})	35.0° (K_d = 76 M^{-1})
0.10[b]	. . .	6.32 ± 0.33[c] (7)	. . .
0.50	3.57 ± 0.12 (8)	6.35 ± 0.26 (3)	10.5 ± 0.5 (7)
0.90	3.63 ± 0.20 (4)	5.29 ± 0.26 (4)	10.7 ± 0.5 (4)
1.35	. . .	6.37 ± 0.39 (10)	. . .
5.00	. . .	6.34 ± 0.18 (3)	. . .
10.0	. . .	6.53	. . .

[a] From eq 5 using the values of K_d cited for each temperature; k_1 and K_d at μ = 1.00 M. [b] This is the formal H^+ concentration; the actual value used in the computation was higher, being corrected for K_a of $HCrO_4^-$. [c] The uncertainty is the average deviation from the mean cited at the particular $[H^+]$ and T for the number of experiments given in parentheses.

TABLE III

SUMMARY OF LEAST-SQUARES FIT OF KINETIC DATA FOR REACTION I

	15.0°		25.0°		35.0°	
	a	*b*	*a*	*b*	*a*	*b*
$10^{-3}k_1$, M^{-1} sec^{-1}	3.98 ± 0.11	3.57 ± 0.15	6.08 ± 0.16	6.35 ± 0.35	10.11 ± 0.04	10.6 ± 0.5
$10^{-5}k_2$, M^{-2} sec^{-1}	4.14 ± 0.12	4.63 ± 0.19	6.48 ± 0.21	6.22 ± 0.34	8.46 ± 0.51	8.0 ± 0.4
K_d, M^{-1}	104 ± 6	129	107 ± 6	98	84 ± 5	76

[a] Least-squares fit to eq 4 with both parameters free to refine to their "best" value. [b] Calculation subject to the constraint $K_d = k_2/k_1$ with K_d held at its known value.

squares parameters are given in Table III, for the computations both where K_d was constrained to its known value and where the rate constant ratio was not so constrained. The parameters were found to agree within two standard deviations. The set with K_d constrained is probably the better representation, since the direct determination of K_d appears more reliable than the kinetic method.

The rate constants were then fit to the Eyring absolute rate theory equation, giving the activation parameters for the forward and reverse rate constants summarized in Table IV. The two different sets of numbers, *i.e.*, with and without the constraint on K_d, agree within two standard deviations, which agreement is taken as evidence of the correctness of the rate and equilibrium studies in describing the nature of such Cr(VI) solutions and the equilibria that pertain.

TABLE IV

ACTIVATION PARAMETERS FOR REACTION I

	Best-fit values[a]	With K_d constrained[b]
$\Delta H_1^{\ddagger}$, kcal mol^{-1}	7.6 ± 0.60	9.0 ± 0.2
$\Delta S_1^{\ddagger}$, cal mol^{-1} deg^{-1}	−15.6 ± 0.2	−11.0 ± 0.5
$\Delta H_2^{\ddagger}$, kcal mol^{-1}	5.7 ± 0.8	4.3 ± 0.5
$\Delta S_2^{\ddagger}$, cal mol^{-1} deg^{-1}	−12.8 ± 2.6	−17.7 ± 1.5

[a] Based on the "best" least-squares values of k_1 and k_2 from Table III. [b] Based on the least-squares values of k_1 and k_2 from Table II calculated with the constraint $K_d = k_2/k_1$.

Interpretation and Discussion

Comparision with Previous Results.—Perlmutter-Hayman and coworkers have studied reaction I by a direct method in the absence of acid catalysts other than H^+ and found $k_1 = 11.3 \times 10^3$ M^{-1} sec^{-1} at 25.0° in 0.20 M sodium nitrate solution.[3b] In the course of studying the general-acid catalysis[3c] by HOAc, extrapolation to [HOAc] = 0 gave $k_1 = 10.5 \times 10^3$ M^{-1} sec^{-1} under the same conditions. Similarly, with chloroacetic acid, the rates extrapolated to $k_1 = 5.5 \times 10^3$ M^{-1} sec^{-1} at 25.0° and 1.0 M ionic strength (sodium nitrate medium).[3c] The latter agrees reasonably well with the result here, $k_1 = 6.35 \times 10^3$ M^{-1} sec^{-1} at 25.0° and 1.0 M ionic strength (lithium perchlorate medium). As pointed out earlier,[3c] the variation of k_1 with ionic strength is consistent with the expected "salt effect" for a second-order reaction of oppositely charged ions.

In solutions of higher pH than those studied here, a rate expression with a zero-order dependence on $[H^+]$ was found.[3,4] The rate constant for the spontaneous (nonacid-catalyzed) dissociation of $Cr_2O_7^{2-}$ is 0.03 sec^{-1} (25.0°, μ = 0.1 M); k_{exptl} for the H^+ independent pathway varies within the limits 0.02–0.09 sec^{-1} over the range of $[HCrO_4^-]$ covered by Swinehart and Castellan.[4] This pathway contributed at most 5% in any of the present experiments and generally much less than that.

Cr(VI)–Oxygen Exchange.—The interconversion of $HCrO_4^-$ and $Cr_2O_7^{2-}$ necessarily accomplishes oxygen exchange between Cr(VI) and water. In fact, in neutral and basic solution both processes have been studied[3,10,11] and found to proceed at identical rates.

The rate of reaction I fixes only a lower limit on the rate of Cr(VI)–oxygen exchange, however, because one or more additional pathways may possibly operate for the exchange reaction. Using an ^{17}O nmr technique Jackson and Taube[12] evaluated the Cr(VI)–H_2O exchange rate in quite concentrated dichromate solutions. They report a rate law $k_{ex}[Cr_2O_7^{2-}][H^+]$ with k_{ex} = 17 × 10^3 M^{-1} sec^{-1} at 20° in 3.1 m $Na_2Cr_2O_7$. Interpolated to 20°, the value of k_1 from the present work is 5 × 10^3 M^{-1} sec^{-1} (1.0 M ionic strength). A quantitative comparison is not reliable because the media are very different, although the concentrated dichromate solution has a higher ionic strength. Extending the known dependence on k_1 to this region (which is highly questionable), one might expect the value of k_{ex} to be smaller than that of k_1 were reaction I the only pathway for oxygen exchange. Tentatively, this indicates exchange also proceeds by a second parallel pathway. This result can only be regarded as tentative, however, because the effect on k_1 of a change in medium from 1 M $LiClO_4$ to 3 m $Na_2Cr_2O_7$ cannot be estimated reliably.

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(10) M. R. Baloga and J. E. Earley, *J. Phys. Chem.*, **67**, 964 (1963).
(11) R. H. Holyer and H. W. Baldwin, *Can. J. Chem.*, **45**, 413 (1967).
(12) J. A. Jackson and H. Taube, *J. Phys. Chem.*, **69**, 1844 (1965).

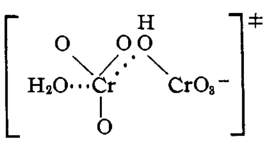
Because Perlmutter-Hayman[3c] has noted general-acid and general-base catalysis of reaction I, the question must be raised of whether $HCrO_4^-$ can, itself, act as such a catalyst. Experimentally, the kinetic data provide no indication of a concentration dependence corresponding to a rate term $k[HCrO_4^-][Cr_2O_7^{2-}]$. Considering the relation between k_{HA} and pK_a in the Brønsted catalysis law and considering the magnitudes of k_{HA} for other acids[3c], $k_{HCrO_4^-}$ might be expected to be of the order of 0.1 M^{-1} sec^{-1}. This would have been entirely negligible in all of the present experiments.

This computation may, however, bear on the question of the relation between the rates of Cr(VI)–H_2O exchange and reaction I. If the enhanced rate found by Jackson and Taube[12] is an authentic "chemical" effect and not simply an unanticipated medium effect, it appears plausible that it might arise from a rate term in which $HCrO_4^-$, present at fairly high concentration in such solutions, acts as an acid catalyst. Further resolution of the situation will await O-17 nmr experiments at lower concentrations or a quenched-flow exchange experiment on the Cr(VI)–H_2O rate in the strongly acidic medium used here.

Mechanism.—The net activation process[18] is given by the equation

$$2HCrO_4^- + H^+ \rightleftharpoons [H_3Cr_2O_8^-]^{\ddagger} \rightleftharpoons Cr_2O_7^{2-} + H_3O^+ \tag{II}$$

The detailed mechanism of the dissociation of $Cr_2O_7^{2-}$ possibly involves the nucleophilic displacement of $HCrO_4^-$ by H_2O with the catalytic proton resident on the bridging oxygen.[3c,14] There is little basis on which to choose between two of the likely structures of the transition state



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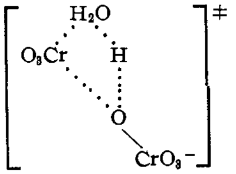

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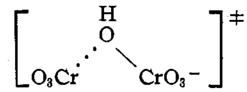

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A transition state such as **3**, with an "anhydride" structure, is deemed less likely, because the necessary dehydration step (reaction III) appears too high in energy to be consistent with the high reaction rate and

$$HCrO_4^- + H^+ \rightleftharpoons CrO_3 + H_2O \tag{III}$$

$$CrO_3 + HCrO_4^- \rightleftharpoons \mathbf{3} \rightleftharpoons Cr_2O_7^{2-} + H^+ \tag{IV}$$

the low activation energy. Nucleophilic attacks with transition states resembling **1** and **2** have been proposed in the earlier studies.[3c,14]

Related Reactions.—The condensations of $HCrO_4^-$ with anions other than itself proceed by similar mechanisms.[14] Interestingly, a kinetic study[15] of the formation of an iron(III)–chromate complex, reaction V, indicated that the mechanism probably involved substitution on Fe(III), not on Cr(VI).[16] In the case of $Cr(H_2O)_6^{3+}$, which is extremely inert to substitution, the formation of the chromato complex does involve Cr(VI) substitution.[17]

$$Fe(H_2O)_6^{3+} + HCrO_4^- = (H_2O)_5FeCrO_4^+ + H_3O^+ \tag{V}$$

In the oxidation of Fe^{2+}, VO^{2+}, and $Ta_6Br_{12}^{2+}$ by $HCrO_4^-$, kinetic terms with a rate dependence on $[HCrO_4^-]^2$ are noted.[18–20] As pointed out by Westheimer[21] this kinetic term is consistent with the oxidation of the metal complexes by $Cr_2O_7^{2-}$ (in parallel to their oxidation by $HCrO_4^-$, which usually constitutes a more important pathway). If the oxidation by Cr(VI) occurred more rapidly than reaction I, it would be possible to do experiments in which the latter equilibrium was not maintained, thereby varying $[HCrO_4^-]$ and $[Cr_2O_7^{2-}]$ independently. This method would, therefore, be capable of providing a direct experimental check of the very reasonable proposal that the second-order dependence on $[HCrO_4^-]$ implicates $Cr_2O_7^{2-}$. As it happens, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are equilibrated *via* reaction I so much more rapidly than they oxidize metal ions yet studied that the direct verification proposed here is not feasible in these systems.

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