243. High-Pressure Stopped-Flow Study of the Kinetics of Base Hydrolysis of the Dichromate Ion by Hydroxide Ion, Ammonia, Water, and 2,6-Lutidine in Aqueous Solution

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Summary

Volumes of activation for the base hydrolysis of the dichromate anion have been measured at 298.2 K, using high-pressure stopped-flow spectrophotometry. The values of ΔV^* ($cm^3 \cdot mol^{-1}$), -17.9 ± 0.6, -19.2 ± 0.9, -24.9 ± 0.9 and -26.0 ± 0.7 for OH^-, NH_3, H_2O and 2,6-lutidine, respectively, are consistent with an interchange mechanism with associative activation mode (I_a).

Previous studies of the kinetics of the hydrolysis of the dichromate ion by a range of bases (B) have established the following general mechanism [1] [2].

$$[Cr_2O_7]^{2-} + B \xrightarrow{\text{slow}} BCrO_3 + [CrO_4]^{2-} \tag{1}$$

$$BCrO_3 + H_2O \xrightarrow{\text{rapid}} BH^+ + [HCrO_4]^- \tag{2}$$

$$[HCrO_4]^- + B \xrightarrow{\text{rapid}} BH^+ + [CrO_4]^{2-} \tag{3}$$

When B is H_2O, *Equilibrium 4* is established.

$$[Cr_2O_7]^{2-} + H_2O \rightleftharpoons 2\,[HCrO_4]^- \tag{4}$$

The kinetics of *Equilibrium 4* can be studied either by the concentration-jump method [3], or the rate of reaction with H_2O obtained by reaction with an excess of a poor nucleophile such as 2,6-lutidine, followed by extrapolation of the observed pseudo-first-order rate constant (k_{obs}) to zero base concentration according to *Equations 5* and *6* [1]:

$$-d[Cr_2O_7^{2-}]/dt = k_{obs}[Cr_2O_7^{2-}] \tag{5}$$

$$k_{obs} = k_{H_2O}[H_2O] + k_B[B] \tag{6}$$

In this work, the kinetics of these reactions were studied by stopped-flow spectrophotometry at variable pressure to determine the volumes of activation, and to see if a similar picture to that deduced from the very negative ΔS^* holds true for the volumes.

Experimental. – The kinetic experiments were run on the high-pressure stopped-flow spectrophotometer described in [4]. The wavelength of observation was 475 nm. All measurements were taken at 298.2 K in aq. solutions of 0.100 M ionic strength (maintained though addition of KNO_3, *Merck, p.a.*). The k_{obs}-values are the average of two to four runs at each pressure. The concentrations refer to values at ambient pressure, without correcting for solution volume changes with pressure [5]. Solutions were made up in N_2-scrubbed deionized water. The chemicals used were: $K_2Cr_2O_7$ *(Baker's Analyzed)*, KOH *(Merck, p.a.)*, NH_3 *(Merck, p.a.)* and 2,6-lutidine *(Fluka, purum)*. The 2,6-lutidine sample was distilled from KOH-pellets shortly before use. Tables of experimental data are available from the authors.

Results. – Reactions were studied under pseudo-first-order conditions, with allowance being made for the rapid consumption of base by the $[HCrO_4]^-$ present *(Equilibrium 4)* as described in [1]. For the reaction with 2,6-lutidine, the variations of k_{obs} with [2,6-lutidine] at eight pressures is shown in *Fig. 1*. The second-order rate constants for the reaction with 2,6-lutidine and with H_2O were obtained by linear least-squares analysis from the slopes and intercepts of the straight lines in *Fig. 1* using *Equation 6*. For each system, the second-order rate constants k are plotted as a function of pressure in *Fig. 2*. Volumes of activation, ΔV^*, were obtained by linear least-squares analysis of these plots using *Equation 7*.

$$\ln(k) = \ln(k_0) - (\Delta V^*/RT)P \tag{7}$$

The variable-pressure results are compared with those from the variable-temperature study in the *Table*. There is good agreement between the k_0- and k-values.

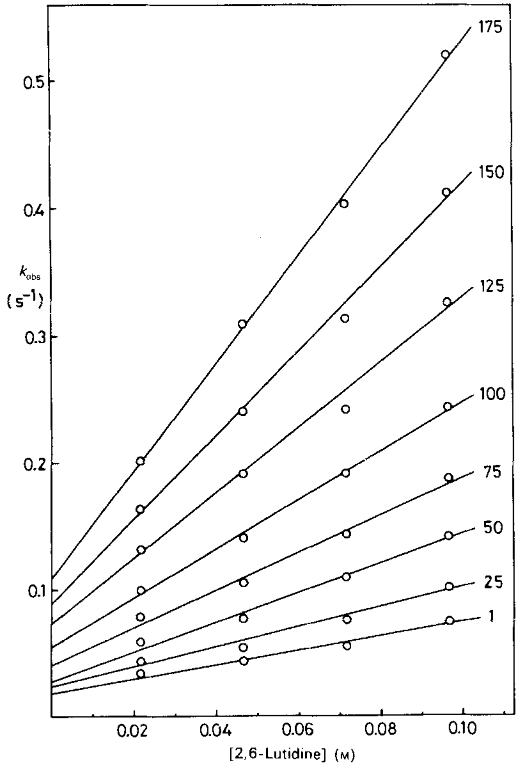

Fig. 1. *Variation of pseudo-first-order rate constants* k_{obs} *with [2,6-lutidine] at various pressures.* T = 298.2 K; Ionic strength = 0.100 M (KNO_3); [Cr(VI)] = $8 \cdot 10^{-3}$ M.

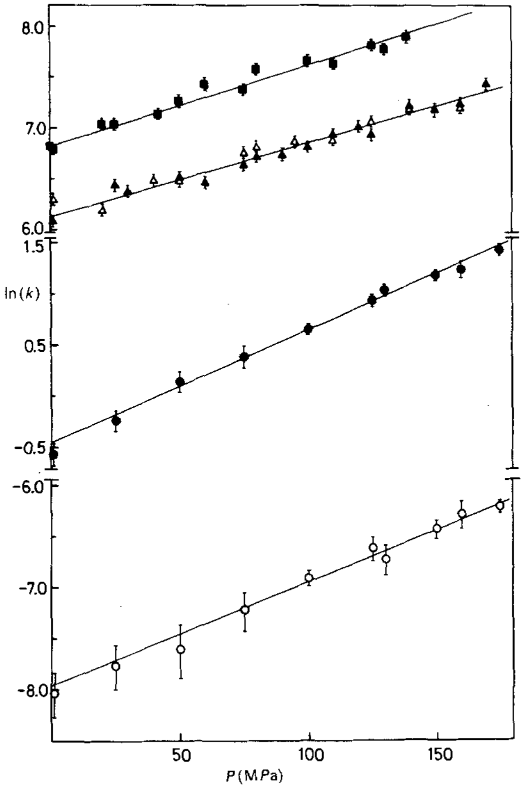

Fig. 2. *Variation of second-order rate constants* k *with pressure.* T = 298.2 K; Ionic strength = 0.100 M (KNO_3); [Cr(VI)] = $8 \cdot 10^{-3}$ M; $k = k_{obs}$/[base] ± 5%. ○ H_2O, from intercepts of k_{obs} *vs.* [2,6-lutidine] and after division by [H_2O] (55 M); ● 2,6-lutidine, from slopes of k_{obs} *vs.* [2,6-lutidine]; [lutidine] = 0.0218, 0.0468, 0.0718 and 0.0968 M. ▲ OH^-, [OH^-] = $1.7 \cdot 10^{-2}$ M; △ OH^-, [OH^-] = $3.7 \cdot 10^{-2}$ M; ■ NH_3, [NH_3] = $1.7 \cdot 10^{-2}$ M.

Table. *Summary of Results* [a])

Base	Variable-pressure work [b])		Variable-temperature work [c])		
	ΔV^* [$cm^3 mol^{-1}$]	k_0 [$M^{-1} s^{-1}$]	k [$M^{-1} s^{-1}$]	ΔH^* [kJ mol^{-1}]	ΔS^* [J $K^{-1} mol^{-1}$]
OH^-	-17.9 ± 0.6	457 ± 12	390	20.5 ± 1.7	-126.4 ± 6.3
NH_3	-19.2 ± 0.9	943 ± 29	860	7.9 ± 1.3	-161.1 ± 4.2
H_2O	-24.9 ± 0.9	$(3.51 \pm 0.20) \times 10^{-4}$	4.6×10^{-4}	36.8 ± 0.4	-184.9 ± 0.9
2,6-Lutidine	-26.9 ± 0.7	0.638 ± 0.028	≈ 0.5	≈ 3.3	≈ -239

[a]) Ionic strength = 0.100 M (KNO_3); 298.2 K.
[b]) This work.
[c]) Ref. [1].

Discussion. – The large negative ΔS^*-values obtained previously [1] were discussed in terms of a bimolecular mechanism for this base hydrolysis reaction. The ΔV^*-values are also large and negative, and parallel the ΔS^*-values. The volume contraction arises from bond formation and from an increased electrostriction on nucleophilic attack, as the delocalized doubly negative charge on the dichromate anion concentrates towards the chromate end on going to the transition state. In *Fig. 3*, the volume profile is shown

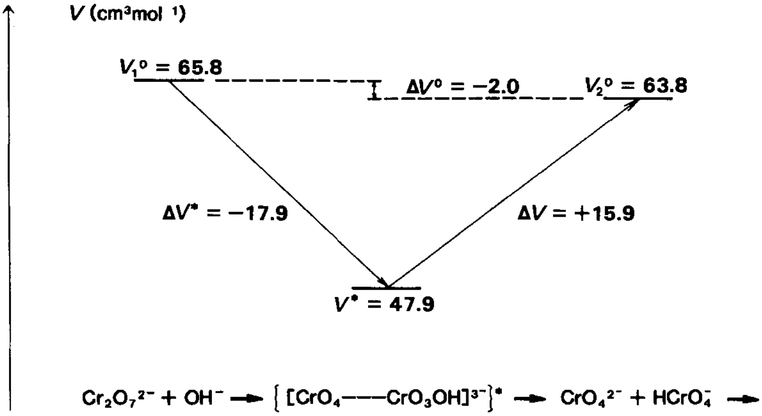

Fig. 3. *Volume profile for the* OH^-*-hydrolysis of* $[CrO_7]^{2-}$ *at 298.2 K.* Partial molar volumes V^0 are referred to $V^0_{H^+} = 0$. $V^0_1 = V^0_{Cr_2O_7^{2-}} + V^0_{OH^-}$; $V^0_2 = V^0_{HCrO_4^-} + V^0_{CrO_4^{2-}}$, $V^0_{Cr_2O_7^{2-}} = +69.8$ cm^3 mol^{-1} [6], $V^0_{OH^-} = -4.0$ cm^3 mol^{-1} [7], $V^0_{CrO_4^{2-}} = +19.7$ cm^3 mol^{-1} [7], $V^0_{HCrO_4^-} = +44.1$ cm^3 mol^{-1} [6].

when the base is OH^-. The volume decreases from 65.8 cm^3 mol^{-1}, the sum of partial molar volumes of the reactants, to 47.9 cm^3 mol^{-1} at the transition state. It then expands to reach 63.8 cm^3 mol^{-1}, the sum of partial molar volumes of the intermediates. The changes in volume (− 17.9, + 15.9) are larger than what can reasonably be expected for a bond-making or bond-breaking process (*ca.* 12 cm^3 mol^{-1} [8]), which shows that, as expected, an electrostrictive contribution is present, even though it does not seem very large. Surprisingly, the change in electrostriction, expected to be somewhat larger for the very compact OH^--anion, is not reflected by a more negative ΔV^*-value for this ion. The partial desolvation of the two strongly H-bonding OH^-- and NH_3-nucleophiles gives a positive contribution to the volume of activation which could explain the more negative ΔV^*-values for H_2O and 2,6-lutidine.

Finally, it should be stressed from the results in the *Table*, that there is no direct correlation between ΔV^* and k.

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