# Kinetics and mechanism of the phosphate-catalyzed heterolysis of the metal–carbon σ bond of α-hydroxyalkyl–chromium(III) complexes. Effects of the non-participating ligands, temperature and pressure

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## Abstract

A detailed kinetic study of the phosphate-catalyzed heterolysis of two α-hydroxyalkyl–chromium(III) complexes, $Cr–CH_2OH^{2+}$ and $Cr–C(CH_3)_2OH^{2+}$, for a series of non-participating ligands was performed Evidence for the formation of phosphate coordinated species is presented. The reported rate and activation parameters demonstrate that the catalytic effect results from *trans*-labilization effects of the coordinated phosphate, which induces a dissociatively activated heterolysis process

*Key words:* Kinetics and mechanism; Chromium complexes; Alkyl complexes

## Introduction

It has been known for quite some time that divalent chromium species in aqueous solution react readily with a variety of aliphatic free radicals to form relatively stable complexes with chromium–carbon σ bonds [1, 2]. These reactions can be initiated via the modified Fenton reaction as indicated in eqn. (1). In general

$$\begin{aligned} &Cr(H_2O)_6^{2+} + H_2O_2 \longrightarrow Cr(H_2O)_6^{3+} + {}^{\cdot}OH + OH^- \\ &{}^{\cdot}OH + RH \longrightarrow {}^{\cdot}R + H_2O \qquad (1) \\ &Cr(H_2O)_6^{2+} + {}^{\cdot}R \longrightarrow (H_2O)_5Cr–R^{2+} + H_2O \end{aligned}$$

such $Cr–R^{2+}$ species can undergo subsequent homolysis and heterolysis reactions. In the presence of an excess $Cr^{2+}$ (to suppress the homolysis reaction), spontaneous heterolysis occurs according to reaction (2) [3, 4]. In more recent studies it was shown that this heterolysis

$$(H_2O)_5Cr–R^{2+} + H_2O \longrightarrow Cr(H_2O)_5OH^{2+} + RH \qquad (2)$$

reaction can by catalyzed by various anions such as $CH_3COO^-$, $CH_3CH_2COO^-$, $HOCH_2COO^-$, $HCOO^-$, $CH_3CH(OH)COO^-$, $ClCH_2COO^-$, $SeO_4^{2-}$, $SO_4^{2-}$ and $H_2PO_4^-$ [3–8]. In a comparative study [8] it was shown that the $CH_3COO^-$ and $H_2PO_4^-$ ions in particular exhibited extremely large catalytic effects. A detailed study of the acetate-catalyzed reaction in which the effects of the non-participating ligands, temperature and pressure were investigated [7], revealed that the catalytic effect results from a *trans*-labilization effect by coordinated acetate and involves attack of a solvent molecule on the metal–carbon bond, presumably according to an $I_d$ mechanism.

Most of the investigated anions [8] are organic in nature and include carboxylate groups that can coordinate to the $Cr–R^{2+}$ species. Of the investigated inorganic anions, $H_2PO_4^-$ seemed to have a very large effect, similar to that of acetate. We have, therefore, undertaken a detailed study of the phosphate-catalyzed reaction and investigated the effects of non-participating ligands, temperature and pressure on the catalyzed heterolysis process. The data enable a detailed analysis of the underlying reaction mechanism and allow a comparison with that reported for the anion-catalyzed reactions [7, 8].

## Experimental

### *Materials*

Chromium(II) solutions were prepared by dissolving chromium metal powder (Aldrich) in 1 M $HClO_4$

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(3 g Cr in 150 ml 1 M $HClO_4$) under Ar atmosphere for 12 h. The Ar was purified from traces of $O_2$ by passing it through a washbottle containing 0.5 M Cr(II) solution. The ligands nta (EGA Chemie) and [15]ane$N_4$ (Aldrich) were used as purchased. Deionized Millipore water was used to prepare all solutions, and all other chemicals were of analytical reagent grade. Solutions were prepared in syringes and deaerated by passing Ar through them for 15 min. Mixing and dilution of the solutions were accomplished with a syringe technique [9], and small glass discs in the syringes were used to mix the solutions. The ionic strength was adjusted with $NaClO_4$ (Merck).

*Measurements*

The Cr(II) concentration was determined spectrophotometrically by following the reduction of $Co(NH_3)_5Cl^{2+}$ at 532 nm ($\epsilon = 49.6$ $M^{-1}$ $cm^{-1}$) [10]. UV–Vis spectra were recorded on Varian CARY 1 and Shimadzu UV-250 spectrophotometers. The pH of the test solutions was measured using a Metrohm 632 instrument under argon atmosphere. Ambient pressure kinetic measurements were performed on a Durrum D110 stopped-flow instrument, whereas experiments at elevated pressure were made using a homemade high-pressure stopped-flow unit [11]. Both instruments were thermostated to ±0.1 °C. Data acquisition and handling were performed on on-line computer systems [12] using the OLIS KINFIT [13] set of programs.

*Production of organochromium complexes*

The organochromium(III) complexes were prepared *in situ* via the modified Fenton reaction. In this procedure a Cr(II) solution containing an alcohol is mixed with an $H_2O_2$ solution. Under these conditions the sequence of reactions (1) occurs [1, 2].

In the present experiments at least a 10% excess of L was employed and phosphate was added to the Cr(II) solution prior to mixing. The rate constant for the reaction of $^{\bullet}OH$ with alcohols is $>8\times10^{8}$ $M^{-1}$ $s^{-1}$ [14], whereas the reaction of $^{\bullet}OH$ with phosphate is considerably slower and does not interfere under the selected experimental conditions. Throughout this study $[Cr(II)] \geqslant 2\times10^{-3}$ and $[H_2O_2] \geqslant 4\times10^{-4}$ M, and since the rate constant for the first step in reaction (1) is $\geqslant 6\times10^{4}$ $M^{-1}$ $s^{-1}$ the formation of the organochromium complex terminates in less than 40 ms. It follows that any heterolysis reaction with a half-life longer than ~50 ms can be studied using this procedure.

## Results and discussion

*Complex formation of $Cr^{2+}$ with $H_2PO_4^-$*

On mixing saturated solutions of $3\times10^{-3}$ M $Cr^{2+}$ and 0.005–0.04 M $H_2PO_4^-$, both at an ionic strength of 0.5 M and pH of 3.8±0.1, a significant decrease in pH to as low as 3.2 is observed (depending on the $[H_2PO_4^-]$ employed). This decrease in pH must be due to the formation of a phosphato complex of $Cr^{2+}$, which will be accompanied by partial deprotonation of the coordinated phosphate ligand as indicated in eqn (3). The p$K_a$ value of $H_2PO_4^-$ is 7.12 and is expected to be a few units lower when $H_2PO_4^-$ is coordinated

$$\begin{tikzcd}[row sep=large] Cr(H_2O)_6^{2+} + H_2PO_4^- \arrow[r, shift left=0.5ex] & Cr(H_2O)_5H_2PO_4^+ + H_2O \arrow[l, shift left=0.5ex] \arrow[d, shift left=0.5ex] \\ & Cr(H_2O)_5HPO_4 + H^+ \arrow[u, shift left=0.5ex] \end{tikzcd} \qquad (3)$$

to Cr(II) (see further 'Discussion'). Binding of phosphate as a bidentate ligand is unlikely since this would involve even more release of $H^+$ ions during complex formation. According to the mentioned decrease in pH only 10–20% of the 1:1 complex actually deprotonates. Experiments could not be performed at a more favourable, higher pH due to the formation of Cr(II)–phosphate precipitates under such conditions. UV–Vis spectra show no significant changes on the addition of $H_2PO_4^-$ to Cr(II) solutions in the range 350–550 nm. Only a small absorbance increase at 650 nm accompanied the complex formation process. In addition, the spectra did not show any evidence for the formation of bridged species as in the case of the acetate complexes of Cr(II) [15].

*Ambient pressure kinetic studies*

The heterolysis reactions of a series of $\alpha$-hydroxyalkyl–chromium(III) complexes $(H_2O)_5Cr{-}R^{2+}$, *trans*-$([15]aneN_4)(H_2O)Cr{-}R^{2+}$ and *cis*-$(nta)(H_2O)Cr{-}R^-$, R = $CH_2OH$ and $C(CH_3)_2OH$, were studied using the stopped-flow technique described above. Solutions containing $3\times10^{-3}$ M $Cr^{2+}$, $3\times10^{-4}$ M $H_2O_2$, 0.25–1.0 M alcohol, $5\times10^{-3}$–0.4 M phosphate and $NaClO_4$ to maintain the ionic strength, were studied systematically. Kinetic traces at 321 nm clearly show the rapid formation of $Cr{-}R^{2+}$ followed by the subsequent heterolysis reaction, for which the rate strongly depends on the phosphate concentration (see Fig. 1). The heterolysis reaction exhibited excellent first-order behaviour for at least three half-lives of the reaction. The dependence of $k_{obs}$ for heterolysis on the $[H_2PO_4^-]$ is reported in Fig. 2, from which it follows that $k_{obs}$ reaches a limiting value at high phosphate concentrations, similar to that reported for the catalytic effect of acetate [7].

According to the equilibrium information given above, at low phosphate concentrations the unsubstituted Cr(II) species will react with the aliphatic free radical $^{\bullet}R$ according to reaction (1). At high phosphate concentrations, the Cr(II) species will be partly present as $Cr(H_2O)_5H_2PO_4^+$ and $Cr(H_2O)_5HPO_4$ which may

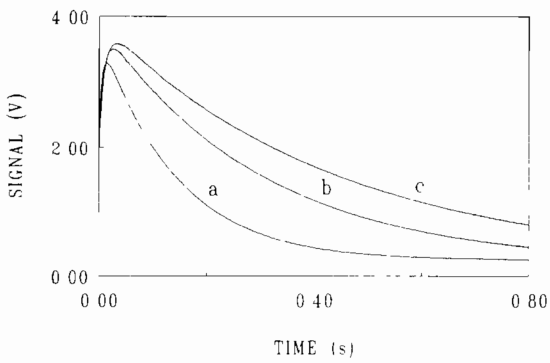


Fig. 1 Typical kinetic traces demonstrating the effect of phosphate on the heterolysis of $(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$ Experimental conditions· $[Cr(II)] = 3.0 \times 10^{-3}$ M; $[H_2O_2] = 3.0 \times 10^{-4}$ M, [i-PrOH] = 0.5 M; ionic strength = 0.5 M, pH = 3 2, absorbance scale, 10 V = 1 absorbance unit, temperature = 25 °C. a, 0 37 M, b, 0.037 M; c, 0.018 M $[H_2PO_4^-]$

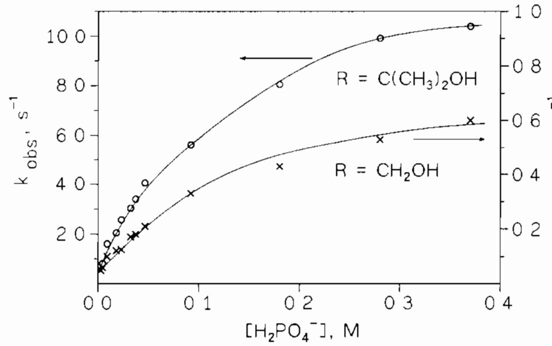


Fig. 2. Plots of $k_{obs}$ vs. $[H_2PO_4^-]$ for the heterolysis of $(H_2O)_5Cr{-}CH_2OH^{2+}$ and $(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$ Experimental conditions $[Cr(II)] = 3.0 \times 10^{-3}$ M, $[H_2O_2] = 3\ 0 \times 10^{-4}$ M, [i-PrOH] = 0.5 M; [MeOH] = 0.5 M, ionic strength = 0 5 M; pH = 3.2, temperature = 25 °C

react with ·R at a different rate to that of the unsubstituted complex. In order to check this, a series of experiments were performed in which phosphate was not added to the Cr(II) solution prior to the formation of $Cr{-}R^{2+}$, but after the formation of $Cr{-}R^{2+}$. The observed kinetic data for the heterolysis reaction were found to be almost a factor 2 smaller than that reported in Fig. 2. Not withstanding this apparent difference, the data clearly demonstrated that the reaction of $H_2PO_4^-$ with $Cr{-}R^{2+}$ is rapid compared to the heterolysis reaction. We can account for this apparent difference in $k_{obs}$ on the basis of a difference in pH between the two procedures, when $H_2PO_4^-$ first coordinates to $Cr^{2+}$ followed by the reaction with ·R, or when $H_2PO_4^-$ coordinates to $Cr{-}R^{2+}$. The p$K_a$ values of coordinated phosphate are expected to be significantly different in these two cases (Cr(II) compared to Cr(III), respectively), and the heterolysis reaction exhibits a significant pH sensitivity. A series of experiments demonstrated that $k_{obs}$ increased exponentially with pH due to the formation of $H_2PO_4^-$ under such conditions (see Fig. 3), from which it follows that the catalytic effect must originate from the interaction of $H_2PO_4^-$ with $Cr{-}R^{2+}$. A similar result was found [16] for the reaction of $(H_2O)_5Cr{-}CH_2CN^{2+}$ with phosphate, in which case $H_2PO_4^-$ and $H_3PO_4$ react at significantly different rates and cause a marked dependence of the process on pH. The pH dependence reported in Fig. 3 suggests that the p$K_a$ value of coordinated $H_2PO_4^-$ could be between 3 and 4, which is within the expected range. In addition, a few experiments were performed as a function of alcohol concentration and the results are summarized in Fig. 4. It follows that the heterolysis rate constant is hardly affected by the [MeOH], but exhibits a significant increase with increasing [i-PrOH]. Since the alcohol is employed to produce the aliphatic free radicals in reaction (1), the observed concentration dependence of the subsequent heterolysis reaction must be related to specific solvation effects in the case of i-PrOH The latter may even involve partial displacement of the coordinated water molecules on Cr(II), and subse-

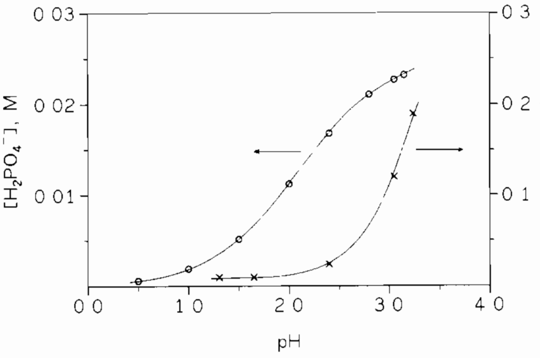


Fig. 3 pH dependence of $k_{obs}$ for the heterolysis of $(H_2O)Cr{-}CH_2OH^{2+}$, correlation with $[H_2PO_4^-]$ in the solution. Experimental conditions $[Cr(II)] = 3\ 0 \times 10^{-3}$ M, $[H_2O_2] = 3.0 \times 10^{-4}$ M; [MeOH] = 0 5 M, [total phosphate] = 0.03 M, ionic strength = 0 5 M, temperature = 25 °C

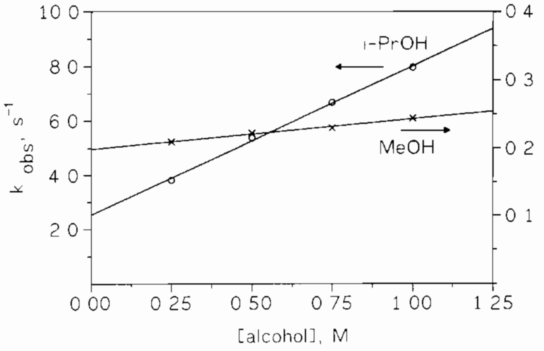
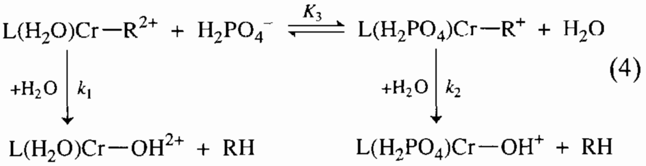


Fig. 4 Effect of alcohol concentration on the heterolysis of $(H_2O)_5Cr{-}CH_2OH^{2+}$ and $(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$ Experimental conditions: $[Cr(II)] = 3\ 0 \times 10^{-3}$ M, $[H_2O_2] = 3.0 \times 10^{-4}$ M, $[H_2PO_4^-] = 0\ 092$ M, ionic strength = 0 5 M, pH = 3 2, temperature = 25 °C

quently on Cr–R$^{2+}$, to result in a more rapid heterolysis reaction.

The observed catalytic effect can be accounted for in terms of the reaction scheme (4), which is similar to that suggested to account for the catalytic effect of a series of anionic species [8], where L = $(H_2O)_4$, or [15]aneN$_4$ and nta for the data reported further on.



$$\begin{tikzcd}
L(H_2O)Cr{-}R^{2+} + H_2PO_4^- \arrow[r, shift left, "K_3"] \arrow[d, "+H_2O\ k_1"'] & L(H_2PO_4)Cr{-}R^{+} + H_2O \arrow[l, shift left] \arrow[d, "+H_2O\ k_2"'] \\
L(H_2O)Cr{-}OH^{2+} + RH & L(H_2PO_4)Cr{-}OH^{+} + RH
\end{tikzcd} \qquad (4)$$

The rate expression in eqn. (5) predicts a linear dependence of $k_{obs}$ on $[H_2PO_4^-]$ at low $[H_2PO_4^-]$ with an intercept $k_1$, i.e. the spontaneous heterolysis reaction in the absence of added phosphate, and slope $k_2K_3$, i.e. the contribution of the catalyzed path. At higher $[H_2PO_4^-]$, eqn. (5) predicts a limiting value for $k_{obs} = k_2$, i.e. when $1 + K_3[H_2PO_4^-] \approx K_3[H_2PO_4^-]$ The data in Fig. 2 can be fitted with a non-linear regression

$$k_{obs} = \frac{k_1 + k_2K_3[H_2PO_4^-]}{1 + K_3[H_2PO_4^-]} \qquad (5)$$

program, where $k_1$ represents the spontaneous and $k_2$ the catalyzed heterolysis reaction path. The values of $k_1$, $k_2$ and $K_3$ are summarized in Table 1, from which it follows that $k_2$ is orders of magnitude larger than $k_1$. The value of $K_3$ is very similar for the two different ·R and predicts that 83% of the Cr–R$^{2+}$ species will be in the $(H_2PO_4)$Cr–R$^+$ form at 0.37 M $H_2PO_4^-$, compared to only 37% at 0.05 M $H_2PO_4^-$. Thus with increasing phosphate concentration the pre-equilibrium in eqn (4) is shifted to the right, and $k_{obs}$ reaches the limiting rate constant $k_2$ at high $H_2PO_4^-$ concentrations.

A similar rate enhancement of the heterolysis of Cr–R$^{2+}$ was observed for the [15]aneN$_4$ system, and the results are summarized in Fig. 5 and Table 1. The $[H_2PO_4^-]$ range was restricted to 0.025 M due to the higher pH. In this system the phosphate ligand must occupy the *trans* position towards the chromium $\sigma$ bond. No significant rate enhancement was found for the nta system (see Fig. 6), in which phosphate must occupy the *cis* position towards the chromium–carbon $\sigma$ bond, even at high phosphate concentrations. On the basis of these experimental observations and the expected trend that metal–carbon $\sigma$ bonds should labilize the *trans* coordination position, it is reasonable to expect that phosphate will mainly occupy the *trans* position in the presence of excess phosphate. Once phosphate is bound it obviously affects the metal–carbon bond strength and causes a *trans*-labilization that will be related to its basicity [8]. This also accounts for the absence of a significant catalytic effect in the case of the nta system. The values of $k_2$ are significantly larger for R = $C(CH_3)_2OH$ than for R = $CH_2OH$, indicating that the metal–carbon bond must be significantly weaker in the former case. For both the aquated and [15]aneN$_4$ systems, the values of $K_3$ are independent of R, but larger in the latter case. This may be related to the expected increase in lability of the axial coordination sites in the [15]aneN$_4$ complex. Thus *trans*-labilization effects of coordinated $H_2PO_4^-/HPO_4^{2-}$ seem to control the catalytic effect on the heterolysis of the chromium–carbon $\sigma$ bond.

A comparison of the $k_2K_3$ values reported in Table 1 with those previously reported for the acetate-catalyzed reaction [7] reveals some very similar trends in both data sets. Both acetate and phosphate have a significantly larger acceleration effect for R = $C(CH_3)_2OH$ than for R = $CH_2OH$. The formation constants $K_3$ are of the same order of magnitude, although the values are significantly higher for the binding of phosphate than for acetate in the case of the aquated Cr(II) system. The values of $K_3$ are very similar for both phosphate and acetate binding to the [15]aneN$_4$ complex. In both cases the nta complex exhibits almost no acceleration in the presence of the anions. It follows from this comparison that acetate and phosphate exhibit a very similar effect in terms of their influence on the heterolysis of the Cr–C bond.

The observed catalytic effect of phosphate reported above is interpreted in terms of mainly a *trans*-labilization effect on the heterolysis reaction. Earlier studies [17, 18] have also reported some *cis*-labilization by

TABLE 1. Rate and equilibrium constants for the spontaneous and phosphate-catalyzed heterolysis of the chromium–carbon $\sigma$ bond at 25 °C[a]

| Complex | $k_1$ ($s^{-1}$) | $k_2$ ($s^{-1}$) | $K_3$ ($M^{-1}$) | $k_2K_3$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|
| $(H_2O)_5Cr{-}CH_2OH^{2+}$ | 0.003 | 0.77 ± 0.05 | 8.0 ± 0.6 | 6.2 ± 0.7 |
| $(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$ | 0.008 | 13.5 ± 0.9 | 8.8 ± 0.4 | 118 ± 8 |
| *trans*-([15]aneN$_4$)$(H_2O)Cr{-}CH_2OH^{2+}$ | 0.006 | 0.88 ± 0.04 | 31.5 ± 0.8 | 28 ± 3 |
| *trans*-([15]aneN$_4$)$(H_2O)Cr{-}C(CH_3)_2OH^{2+}$ | 0.032 | 17.3 ± 0.2 | 50.4 ± 2.1 | 872 ± 12 |
| *cis*-(nta)$(H_2O)Cr{-}C(CH_3)_2OH^-$ | 0.005 | 0.017 ± 0.004 | 15.6 ± 0.3 | 0.27 ± 0.04 |

[a] Experimental conditions: $[Cr(II)] = 3.0 \times 10^{-3}$ M; $[H_2O_2] = 3 \times 10^{-4}$ M, ionic strength = 0.5 M.

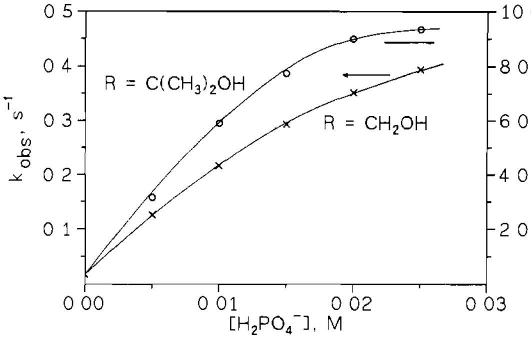


Fig 5. Plots of $k_{obs}$ vs. $[H_2PO_4^-]$ for the heterolysis of ([15]ane$N_4$)($H_2O$)Cr–$CH_2OH^{2+}$ and ([15]ane$N_4$)($H_2O$)Cr–$C(CH_3)_2OH^{2+}$. Experimental conditions: $[Cr(II)] = 3.0 \times 10^{-3}$ M; $[H_2O_2] = 3.0 \times 10^{-4}$ M; [MeOH] = 0.25 M, [i-PrOH] = 0.25 M, [[15]ane$N_4$] = $3.2 \times 10^{-3}$ M; ionic strength = 0.5 M; pH = 3 6; temperature = 25 °C.

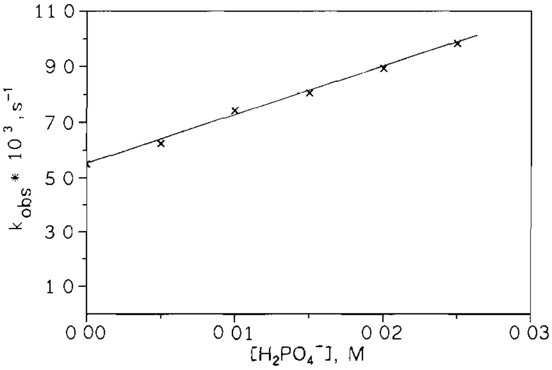


Fig 6. Plot of $k_{obs}$ vs. $[H_2PO_4^-]$ for the heterolysis of (nta)($H_2O$)Cr–$C(CH_3)_2OH^{2+}$ Experimental conditions: $[Cr(II)] = 3.0 \times 10^{-3}$ M; $[H_2O_2] = 3.0 \times 10^{-4}$ M; [i-PrOH] = 0.25 M; [nta] = $3.3 \times 10^{-3}$ M, ionic strength = 0.5 M; pH = 3.6.

anions such as sulfite, nitrate, iodide, bromide, chloride and thiocyanate. The large difference found for the [15]ane$N_4$ and nta systems in the present study indicate that *trans* effects are of more importance than *cis* effects in the present study. This is most probably due to the presence of a metal–carbon bond that causes very significant *trans*-labilization and controls the binding of the phosphate ion, which was not the case in the earlier studies [17, 18].

*Temperature and pressure dependent data*

The temperature dependence of the heterolysis of the Cr–$R^{2+}$ species was studied for the aquated and [15]ane$N_4$ systems at different phosphate concentrations in order to distinguish between the activation parameters for $k_2K_3$ and $k_2$ at low and high phosphate concentrations, respectively. The results are summarized in Table 2 and indicate that the values of $\Delta S^{\neq}$ are all significantly negative, even at the limiting case where $k_{obs} = k_2$. Thus bond formation with the entering solvent molecule must lead to a more ordered transition state during the heterolysis of the chromium–carbon $\sigma$ bond. This is thought to involve direct attack at this bond.

The pressure dependence of the heterolysis reaction was studied under a variety of conditions and the results are summarized in Table 3. The $\Delta V^{\neq}$ data are significantly positive under all conditions and show a decrease to smaller values with increasing phosphate concentration. The latter effect can be as large as 5 to 7 $cm^3$ $mol^{-1}$, which indicates that $\Delta V(K_3)$ must represent this quantity. In terms of the general mechanism in eqn. (4), this step involves the displacement of a coordinated water molecule by $H_2PO_4^-$, which is accompanied by charge neutralization and an overall volume increase. The $\Delta V^{\neq}$ values at high $H_2PO_4^-$ concentrations are all significantly positive and demonstrate that the catalyzed heterolysis reaction follows a dissociatively activated mechanism, most probably of the $I_d$ type based on the magnitude of $\Delta V^{\neq}$ and the negative $\Delta S^{\neq}$ values [19, 20]. The data in Table 3 also demonstrate that there is a minor dependence of $\Delta V^{\neq}$ on the alcohol concentration. Thus the solvation effects reported in Fig. 4 for i-PrOH do not have a major influence on the value of $\Delta V^{\neq}$.

The reported activation parameters in Tables 2 and 3 are also in very close agreement with those previously reported for the acetate-catalyzed reaction [7]. Even

TABLE 2. Rate and activation parameters for the heterolysis of $\alpha$-hydroxyalkyl–chromium(III)[a]

| Complex | $[H_2PO_4^-]$ (M) | $k_{obs}$ at 25 °C ($s^{-1}$) | $\Delta H^{\neq}$ (kJ $mol^{-1}$) | $\Delta S^{\neq}$ (J(K $mol)^{-1}$) |
|---|---|---|---|---|
| $(H_2O)_5Cr–CH_2OH^{2+b}$ | 0.37 | 0.58 | 59±2 | −52±6 |
| | 0.034[d] | 0.18 | 60±4 | −60±13 |
| | 0.014 | 0.10 | 43±3 | −122±8 |
| $(H_2O)_5Cr–C(CH_3)_2OH^{2+b}$ | 0.37 | 12.4 | 34±1 | −111±4 |
| | 0.034[d] | 3.03 | 60±3 | −34±10 |
| | 0.014 | 2.35 | 45±3 | −88±9 |
| *trans*-([15]ane$N_4$)($H_2O$)Cr–$CH_2OH^{2+c}$ | 0.014 | 0.41 | 50±4 | −84±14 |
| *trans*-([15]ane$N_4$)($H_2O$)Cr$C(CH_3)_2OH^{2+c}$ | 0.014 | 7.74 | 38±3 | −99±10 |

[a]Experimental conditions: $[Cr(II)] = 3.0 \times 10^{-3}$ M; $[H_2O_2] = 3.0 \times 10^{-4}$ M; $\mu = 0.5$ M; [(15)ane$N_4$] = $3.2 \times 10^{-3}$ M. [b]pH = 3.2, [alcohol] = 0.25 M. [c]pH = 3.7, [alcohol] = 0.25 M. [d]pH = 3.2; [alcohol] = 0.5 M.

TABLE 3 Volumes of activation for the heterolysis of α-hydroxylalkyl–chromium(III) at 25 °C[a]

| L | $[H_2PO_4^-]$ (M) | pH | [i-PrOH] (M) | [MeOH] (M) | $\Delta V^{\neq}$ ($cm^3\ mol^{-1}$) |
|---|---|---|---|---|---|
| $H_2O$ | 0.37 | 3.2 | 0.5 | | $+11.5\pm0.8$ |
| | 0.018 | 3.2 | 0.5 | | $+15.5\pm0.3$ |
| | 0.37 | 3.2 | 0.25 | | $+16.7\pm0.5$ |
| | 0.018 | 3.2 | 0.25 | | $+15.0\pm0.7$ |
| | 0.092 | 3.2 | 0.25 | | $+13.0\pm0.3$ |
| | 0.092 | 3.2 | 0.50 | | $+15.0\pm0.4$ |
| | 0.092 | 3.2 | 0.75 | | $+14.6\pm0.5$ |
| | 0.092 | 3.2 | 1.0 | | $+18.2\pm1.1$ |
| | 0.37 | 3.2 | | 0.5 | $+9.3\pm0.7$ |
| | 0.18 | 3.2 | | 0.5 | $+11.4\pm2.6$ |
| | 0.092 | 3.2 | | 0.5 | $+14.2\pm1.0$ |
| | 0.032 | 3.2 | | 0.5 | $+13.3\pm0.7$ |
| | 0.018 | 3.2 | | 0.5 | $+13.6\pm0.4$ |
| | 0.37 | 3.2 | | 1.0 | $+16.4\pm0.4$ |
| | 0.37 | 3.2 | | 0.25 | $+10.4\pm0.4$ |
| | 0.018 | 3.2 | | 0.25 | $+15.6\pm0.6$ |
| $[15]aneN_4$ | 0.014 | 3.6 | | 0.25 | $+6.9\pm0.4$ |
| | 0.014 | 3.6 | 0.25 | | $+10.4\pm0.3$ |
| nta | 0.014 | 3.6 | 0.25 | | $+10.2\pm1.0$ |

[a] Experimental conditions. $[Cr(II)]=3.0\times10^{-3}$ M, $[H_2O_2]=3.0\times10^{-4}$ M, $[nta]=3.3\times10^{-3}$ M, $[[15]aneN_4]=3.2\times10^{-3}$ M, ionic strength = 0.5 M

the trends in $\Delta V^{\neq}$ on increasing the anion concentration in the absence and presence of chelating ligands are very similar and demonstrate that the same mechanism must be operative.

We conclude that all the measured activation volumes support a dissociatively activated heterolysis reaction for the phosphate induced process and can be related to the *trans*-labilization effect of coordinated phosphate. The values are significantly more positive than the almost zero values reported for the spontaneous heterolysis reactions for which volume changes associated with bond formation and bond breakage cancel out [21]. Thus *trans*-labilization in the phosphate-catalyzed pathway must account for the increase in $\Delta V^{\neq}$ and the operation of a dissociative mechanism

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