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Identical kinetic behavior of dichromates and halochromates of heterocyclic bases: oxidations of pentan-1-ol

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ABSTRACT: The oxidations of pentan-1-ol with 12 dichromates, fluorochromates, chlorochromates and bromochromate of heterocyclic bases in acidic medium exhibit identical kinetic behavior; first order each with respect to the chromium(VI) reagents and alcohol, and are acid catalyzed. The Arrhenius plots show two common points of intersection, one by the three quinolinium complexes and the other by the rest, suggesting the involvement of the quinolinium moiety in the transition state to be different from that of the other heterocyclic bases. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: chromium(VI) reagents; oxidation; kinetics; pentan-1-ol

INTRODUCTION

Various chromium(VI) reagents, such as pyridinium dichromate (PDC),[1] quinolinium dichromate (QDC),[2] imidazolium dichromate (IDC),[3] 3-carboxypyridinium dichromate (3CPDC),[4] 4-carboxypyridinium dichromate (4CPDC),[4] pyridinium fluorochromate (PFC),[5] quinolinium fluorochromate (QFC),[6] imidazolium fluorochromate (IFC),[7] pyridinium chlorochromate (PCC),[8] quinolinium chlorochromate (QCC)[9] and pyridinium bromochromate (PBC),[10] are used as reagents in organic synthesis. They are capable of effecting chemospecific, regiospecific and stereospecific oxidations in highly sensitive systems.[11–13] Kinetic and mechanistic studies with these reagents in aqueous acetic acid are numerous and so are those dealing with the structure–reactivity relationships operating in these oxidations.[14,15] However, the literature lacks reports on comparisons of the reaction rates and kinetic orders of oxidations of a substrate with these reagents, which is the subject of this work. Since the chromium(VI) oxidation of alcohols is a well studied reaction, pentan-1-ol was selected as the model substrate for this study.[11–14] The results reveal identical kinetic behavior of dichromates and halochromates of heterocyclic bases in the oxidations of pentan-1-ol.

EXPERIMENTAL

PDC,[1] QDC,[2] IDC,[3] 3CPDC,[4] 4CPDC,[4] PFC,[5] QFC,[6] IFC,[7] PCC,[8] QCC,[9] PBC[10] and pentaamminechlorocobalt(III) chloride[16] were prepared as reported. Pentan-1-ol was distilled before use. Acetic acid was refluxed over chromium(VI) oxide for 6 h and distilled through a column. All the chemicals used were of analytical grade. Solutions of chromium(VI) reagents were prepared and standardized iodimetrically. Kinetic measurements were made at constant temperature. Required volumes of the reagents of desired concentrations were mixed, and the progress of the oxidation was followed spectrophotometrically at 350 nm, the wavelength at which all the chromium(VI) reagents exhibit maximum absorbance; the concentrations of the chromium(VI) complexes were restricted to the Beer–Lambert law limit. Pentanal, by its IR spectrum (CCl_4, 1711 cm^{-1}) and the 2,4-dinitrophenylhydrazone derivative, and hexaaquachromium(III) ion, by the UV–visible spectra of the reaction solutions after completion of the oxidation (568 and 406 nm), were identified as the reaction products. Hence the reaction is represented as

$$2\mathrm{Cr(VI)} + 3\mathrm{CH_3(CH_2)_3CH_2OH} \\ \rightarrow 2\mathrm{Cr(III)} + 3\mathrm{CH_3(CH_2)_3CHO} + 6\mathrm{H^+}$$

RESULTS AND DISCUSSION

The oxidations of pentan-1-ol with potassium dichromate (dichromate, DC), PDC, QDC, IDC, 3CPDC, 4CPDC, PFC, QFC, IFC, PCC, QCC and PBC in 30% (v/v) aqueous acetic acid, studied under pseudo-first-order conditions with $[HClO_4]$ and $[\text{alcohol}] \gg [\mathrm{Cr(VI)}]$, are first order with respect to the chromium(VI) reagents.

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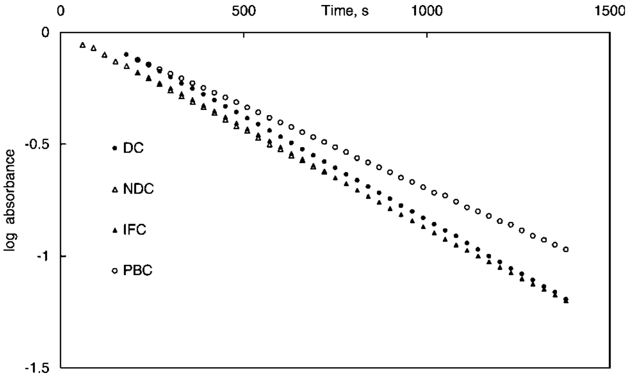

Figure 1. Oxidations of pentan-1-ol with chromium(VI) reagents: pseudo-first-order plots $\{10^3[\text{Cr(VI)}]_0 = 1.0\ \text{g atom dm}^{-3},\ 10^2[\text{alcohol}] = 5.0\ \text{mol dm}^{-3},\ [\text{HClO}_4] = 1.0\ \text{mol dm}^{-3}$, 30% (v/v) aqueous acetic acid, 35 °C$\}$

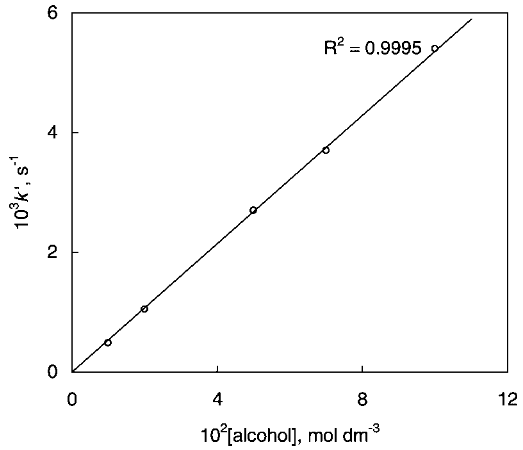

Figure 2. IDC oxidation of pentan-1-ol: linear variation of k' with [alcohol] $\{10^4[\text{Cr(VI)}]_0 = 2.0\ \text{g atom dm}^{-3},\ [\text{HClO}_4] = 1.0\ \text{mol dm}^{-3}$, 30% (v/v) aqueous acetic acid, 35 °C$\}$

Plots of log (absorbance) versus reaction time are linear (e.g. Fig. 1), the least-squares slopes afford the pseudo-first-order rate constants (k'). The pseudo-first-order rate constants decrease with increasing $[\text{Cr(VI)}]_0$, as reported elsewhere.[17–19] The reported explanation for the decrease in the specific reaction rate with increasing $[\text{Cr(VI)}]_0$ is the dimerization of chromium(VI); monochromate is more reactive than dichromate. However, calculation reveals that on increasing the concentration of dichromate from 5.0×10^{-5} to $5.0 \times 10^{-4}\ \text{mol dm}^{-3}$, the concentration of the dimer in the reaction solution increases from 1 to 5% only but the specific rate decreases to two-thirds of its value (Table 1). The former finding is supported by the UV–visible spectral data; the absorbance at 440–450 nm, which is characteristic of the dimer, is insignificant throughout the concentration range studied and the absorbance at 350 nm, which corresponds to the monomer, conforms to the Beer–Lambert law. Hence dimerization is unlikely to be the reason for the large decrease in the specific rate with increasing $[\text{Cr(VI)}]_0$. A possible explanation is that the increase in $[\text{Cr(VI)}]_0$ may lead to some sort of weak association among the monomers resulting in a reactivity decrease. The oxidations are first order with respect to the alcohol. Plots of k' versus [alcohol] are straight lines passing through the origin with correlation coefficients (r) of 0.99 and standard deviations (SD) not larger than 3.8×10^{-4} (e.g. Fig. 2). Table 1 presents the rate data. The reactions are acid catalyzed. The variation of k' with $[\text{HClO}_4]$ appears to be more parabolic than linear (e.g. Fig. 3). In the absence of mineral acid (pH 1.74), the

Table 1. Pseudo-first-order rate constants for oxidation of pentan-1-ol with chromium(VI) reagents in 30% (v/v) aqueous acetic acid at 35 °C

$10^4[\text{Cr(VI)}]_0$ (g atom dm^{-3})	10^2[alcohol] (mol dm^{-3})	[HClO$_4$] (mol dm^{-3})	$10^3k'$ (s^{-1})											
			DC	PDC	QDC	IDC	3CPDC	4CPDC	PFC	QFC	IFC	PCC	QCC	PBC
1.0	5.0	1.00	2.6	3.1	2.3	2.8	2.7	3.2	2.5	1.79	2.6	2.2	1.82	2.1
4.0	5.0	1.00	2.4	2.3	1.80	2.5	2.2	2.3	2.5	1.42	2.3	1.87	1.53	1.86
10.0	5.0	1.00	2.1	1.94	1.53	2.2	2.0	2.2	1.99	1.03	2.0	1.47	1.40	1.69
2.0	1.0	1.00	0.34	0.41	0.39	0.49	0.47	0.45	0.46	0.28	0.42	0.36	0.28	0.35
2.0	2.0	1.00	0.69	0.90	0.66	1.05	1.00	0.77	0.79	0.58	0.96	0.67	0.76	0.65
2.0	7.0	1.00	2.8	3.5	2.8	3.7	4.1	3.6	3.8	2.5	3.2	3.0	2.6	2.5
2.0	10.0	1.00	4.4	6.1	4.9	5.4	5.6	5.0	5.3	3.1	5.8	4.1	3.7	4.3
2.0	5.0	0.10	0.096	0.128	0.162	0.160	0.099	0.148	0.148	0.115	0.134	0.140	0.113	0.091
2.0	5.0	0.20	0.26	0.28	0.31	0.31	0.23	0.29	0.28	0.199	0.26	0.21	0.181	0.186
2.0	5.0	0.40	0.57	0.61	0.68	0.84	0.60	0.76	0.77	0.44	0.51	0.53	0.38	0.52
2.0	5.0	0.60	0.93	0.94	1.09	1.25	1.06	1.02	1.03	0.74	1.15	0.74	0.72	0.76
2.0	5.0	1.00	2.4	2.9	1.9	2.7	2.5	2.3	2.6	1.66	2.4	2.0	1.44	1.96
2.0[a]	5.0	1.00	1.6	1.48	1.07	1.45	1.44	1.66	1.43	1.06	1.42	1.39	1.09	1.41
2.0[b]	5.0	1.00	2.2	2.4	1.82	2.5	2.6	2.5	2.4	1.80	2.4	2.2	1.77	2.2
2.0[c]	5.0	1.00	2.5	3.0	2.4	3.0	2.7	2.7	3.0	2.1	2.3	2.5	1.69	2.3

[a] $[\text{Mn}^{2+}] = 0.020\ \text{mol dm}^{-3}$.
[b] $[\text{acrylamide}] = 0.10\ \text{mol dm}^{-3}$.
[c] $[\text{SDS}] = 0.050\ \text{mol dm}^{-3}$.

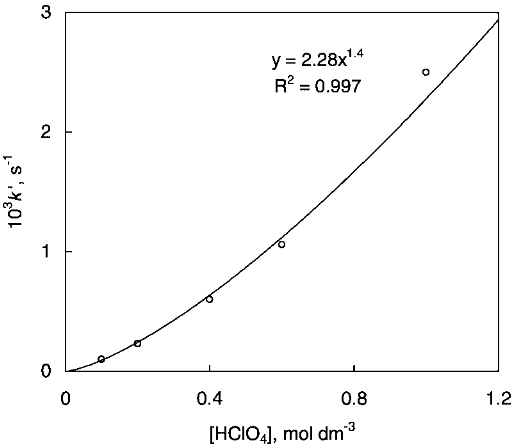

Figure 3. 3CPDC oxidation of pentan-1-ol: dependence of k' on $[HClO_4]$ $\{10^4[Cr(VI)]_0 = 2.0$ g atom dm^{-3}, 10^2[alcohol] = 5.0 mol dm^{-3}, 30% (v/v) aqueous acetic acid, 35 °C}

oxidations are too slow to follow. Added manganese(II) ion inhibits the reactions. Anionic micelles of sodium dodecyl sulfate (SDS) have no influence on the oxidation rates. Acrylamide, a vinyl monomer, fails to suppress the reactions. Also, reaction solutions do not initiate polymerization of acrylamide, thus excluding the possibility of a radical mechanism.

In aqueous and partly aqueous media, dichromate is hydrolyzed and in acidic medium the chromium(VI) species are[20] $Cr_2O_7^{2-}$, $HCr_2O_7^-$, $H_2Cr_2O_7$, CrO_4^{2-}, $HCrO_4^-$ and H_2CrO_4. Calculation of $[Cr_2O_7^{2-}]$ shows that 95–99% of the dimer is hydrolyzed in the concentration range 5.0×10^{-4}–5.0×10^{-5} mol dm^{-3} of dichromate. The UV–visible spectra of the chromium(VI) reagents in the reaction solution but in the absence of alcohol confirm the same; the absorbance near 440 is insignificant. $H_2Cr_2O_7$ is a strong acid and is almost completely ionized. Also, the concentration of hydrogen dichromate relative to dichromate anion ($[HCr_2O_7^-]/[Cr_2O_7^{2-}]$), deduced using the dissociation constant of hydrogen dichromate,[20] shows a negligible concentration of hydrogen dichromate. Calculation of the concentration of chromate anion relative to hydrogen chromate ($[CrO_4^{2-}]/[HCrO_4^-]$) shows that chromate anion is not present at the experimental acidity. The concentration of chromic acid relative to hydrogen chromate ($[H_2CrO_4]/[HCrO_4^-]$), obtained using the reported dissociation constant,[20] increases from 0.033 to 0.20 when $[HClO_4]$ is increased from 0.10 to 1.00 mol dm^{-3}; in the absence of mineral acid, the value is very low (3.5×10^{-3}). The above calculations reveal that the most abundant chromium(VI) species in the reaction medium is hydrogen chromate. However, at high acidities, chromic acid is also present in comparable concentrations. Solvents of high permittivity favor dissociation of ionic complexes and similar speciation is likely in PDC, QDC, IDC, 3CPDC and 4CPDC; the permittivity of the reaction medium (calculated) is 56.8. Fluorochromate, chlorochromate and bromochromate anions ($XCrO_3^-$; X = F, Cl, Br) are probably the predominant species in the case of monomers. In acidic solutions the halogens of the halochromates are labile, resulting in the formation of hydrogen chromate and chromic acid.[21] Chemical tests support the same; silver nitrate precipitates silver halides from aqueous acidic solutions of chlorochromates and bromochromate; the precipitation is instantaneous in the case of PCC but is slow with QCC and PBC.

The oxidations are first order in the chromium(VI) reagents and alcohol and is acid catalyzed. In highly acidic medium, chromic acid is protonated and the apparent parabolic dependence of k' on $[HClO_4]$ reveals the involvement protonated chromic acid ($H_3CrO_4^+$) in the oxidation. In the case of monomers, it may even be protonated halochromic acids ($H_2XCrO_3^+$; X = F, Cl, Br). However, it is possible that chromic acid or halochromic acid and hydrogen chromate or halochromate ($HXCrO_3$ and $XCrO_3^-$; X = OH, F, Cl, Br) also act as oxidizing species. The UV–visible spectra of the chromium(VI) reagents, the chromium(VI) reagents with mineral acid and the reaction solutions show no complex formation between the alcohol and the chromium(VI) species. Hence the possible mechanism involves the rate-determining oxidation of the alcohol with $H_2XCrO_3^+$, $HXCrO_3$ and $XCrO_3^-$. In the rate-limiting step, chromium(IV) is formed.[12,13] This is confirmed by the experimental observation that manganese(II) ion suppresses the oxidation. Manganese(II) ion reduces the chromium(IV) formed to chromium(III) ion and is oxidized to manganese(III).[22] In the absence of manganese(II) ions, chromium(IV) reduces chromium(VI) to chromium(V); the oxidation of alcohol with chromium(V) is fast.[12,13] Although the reduction potentials of chromium(VI) ($Cr_2O_7^{2-}/Cr^{3+}$) and manganese(IV) (MnO_2/Mn^{2+}) in acidic solution are 1.33 and 1.23 V, respectively, a separate experiment reveals that the reduction of chromium(VI) with manganese(II) under the experimental conditions is kinetically inert. In recent years, a mechanism involving chromium(II), also as an intermediate, has been suggested.[22] The chromium(IV) formed oxidizes the organic substrate and is reduced to chromium(II); chromium(II) reduces chromium(VI) yielding chromium(III) and chromium(V). The ambiguity in the reaction mechanism was resolved by testing for the transient chromium(II) with pentaamminechlorocobalt(III).[23] The reaction was carried out in the presence of 0.015 mol dm^{-3} pentaamminechlorocobalt(III) chloride, $[Co(NH_3)_5Cl]Cl_2$, and the absence of reduction of cobalt(III) to cobalt(II), confirmed by the lack of absorbance of $CoCl_4^{2-}$ at 692 nm[24] in the reaction solution diluted 10-fold with concentrated HCl, excludes the presence of transient chromium(II). Hence the chromium(IV) formed is not reduced to chromium(II) by pentan-1-ol.

$$XCrO_3^- + H^+ \rightleftharpoons HXCrO_3 \qquad K_1$$

$$HXCrO_3 + H^+ \rightleftharpoons H_2XCrO_3^+ \qquad K_2$$

$$H_2XCrO_3^+ + RCH_2OH \rightarrow RCHO + HXCrO_2 + H_3O^+ \qquad k_3$$

$$HXCrO_3 + RCH_2OH \rightarrow RCHO + HXCrO_2 + H_2O \qquad k_4$$

$$XCrO_3^- + RCH_2OH \rightarrow RCHO + XCrO_2^- + H_2O \qquad k_5$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(VI)} \rightarrow 2\ \mathrm{Cr(V)} \qquad \text{fast}$$

$$\mathrm{Cr(V)} + RCH_2OH \rightarrow RCHO + \mathrm{Cr(III)} + 2H^+ \qquad \text{fast}$$

where X = OH, F, Cl, Br. The rate law for the proposed mechanism is

$$\begin{aligned} -\mathrm{d[Cr(VI)]}/\mathrm{d}t = &\{2(K_1K_2k_3[H^+]^2 + K_1k_4[H^+] + k_5)/ \\ &(1 + K_1[H^+] + K_1K_2[H^+]^2)\} \\ &[\mathrm{alcohol}][\mathrm{Cr(VI)}] \end{aligned} \qquad (1)$$

and the pseudo-first order rate constant is

$$\begin{aligned} k' = &\{2(K_1K_2k_3[H^+]^2 + K_1k_4[H^+] + k_5)/ \\ &(1 + K_1[H^+] + K_1K_2[H^+]^2)\}[\mathrm{alcohol}] \end{aligned} \qquad (2)$$

With the approximation $1 + K_1[H^+] \gg K_1K_2[H^+]^2$, Eqn (2) simplifies to

$$\begin{aligned} k' = &\{2(K_1K_2k_3[H^+]^2 + K_1k_4[H^+] + k_5)/ \\ &(1 + K_1[H^+])\}[\mathrm{alcohol}] \end{aligned} \qquad (3)$$

With the available experimental data, application of non-linear regression to verify the simplified rate Eqn (3) may not provide significant results. Non-linear regression and multiple linear regression form a common component of software designed for the evaluation of experimental data and Eqn (3) may be rearranged for application of multiple linear regression:

$$\begin{aligned} k'(1 + K_1[H^+]) = &\ 2(K_1K_2k_3[H^+]^2 \\ &+ K_1k_4[H^+] + k_5)[\mathrm{alcohol}] \end{aligned} \qquad (4)$$

Since the pK_a value of chromic acid in 30% aqueous acetic acid at 35 °C is unavailable, as an approximation the value at 25 °C in aqueous solution was used for the verification of the rate law;[20] the influence of the heterocyclic bases on the pK_a of chromic acid is ignored. Multiple linear regressions of the rates of all 12 chromium(VI) reagents studied reveal that only $H_3CrO_4^+$ makes itself felt in the oxidation; the oxidations by H_2CrO_4 and $HCrO_4^-$ are insignificant. This is as expected as the protonated chromic acid is a more potent oxidant than chromic acid and hydrogen chromate. Hence the kinetic expression (4) further simplifies to

$$k'(1 + K_1[H^+]) = 2K_1K_2k_3[H^+]^2[\mathrm{alcohol}] \qquad (5)$$

Table 2. Activation parameters for the oxidations of pentan-1-ol with chromium(VI) reagents $\{10^4[\mathrm{Cr(VI)}]_0 = 2.0\ \mathrm{g\ atom\ dm^{-3}},\ 10^2[\mathrm{alcohol}]_0 = 5.0\ \mathrm{mol\ dm^{-3}},\ [\mathrm{HClO_4}] = 1.0\ \mathrm{mol\ dm^{-3}}$, 30% (v/v) aqueous acetic acid}

Reagent	$10^2K_1K_2k_3$ ($\mathrm{dm^9\ mol^{-3}\ s^{-1}}$)[a]	E_a ($\mathrm{kJ\ mol^{-1}}$)	Log$A$
DC	2.64 ± 0.06	38.7 ± 0.0	3.9 ± 0.0
PDC	3.29 ± 0.12	22.4 ± 2.2	1.2 ± 0.4
QDC	2.58 ± 0.12	19.2 ± 1.9	0.6 ± 0.3
IDC	3.19 ± 0.06	28.5 ± 0.5	2.3 ± 0.1
3CPDC	3.24 ± 0.09	34.9 ± 0.0	3.3 ± 0.0
4CPDC	2.96 ± 0.06	35.4 ± 0.1	3.4 ± 0.0
PFC	3.13 ± 0.06	31.1 ± 0.2	2.7 ± 0.0
QFC	1.96 ± 0.06	29.0 ± 0.7	2.1 ± 0.1
IFC	3.11 ± 0.11	32.5 ± 2.7	2.9 ± 0.5
PCC	2.47 ± 0.05	44.1 ± 1.3	4.8 ± 0.2
QCC	2.12 ± 0.06	43.8 ± 1.7	4.6 ± 0.3
PBC	2.42 ± 0.07	43.5 ± 1.0	4.7 ± 0.2

[a] 35 °C.

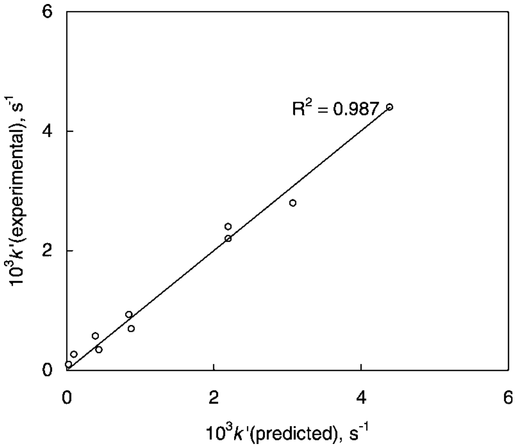

Figure 4. DC oxidation of pentan-1-ol: graphical dependence of k'(experimental) on k'(predicted) (number of data sets, $n = 11$; conditions as in Table 1)

Analysis of the rate data using multiple linear regression confirms the simplified kinetic expression (5) and yields the values of $K_1K_2k_3$ (Table 2). Figure 4 shows the graphical dependence of the experimental k' on the predicted k'; 11 data sets were used for the multiple linear regression. Variation of the specific reaction rate in chromium(VI) with $[\mathrm{Cr(VI)}]_0$ is well known[17–19] and hence the k' values at the extreme $[\mathrm{Cr(VI)}]_0$ were not included in the regression; nor were the specific rates in the presence of the chromium(IV) scavenger Mn^{2+} and also in micellar medium. Since the kinetic data for all 12 chromium(VI) reagents conform to the rate law in Eqn (5) using the same K_1 value of hydrogen chromate, the oxidations turn out to be chromic acid oxidation; the influence of the heterocyclic bases on the rate and mechanism of the oxidation is insignificant or minor.

The reaction rates at 20–50 °C afford the activation energies of the acid-catalyzed oxidations under

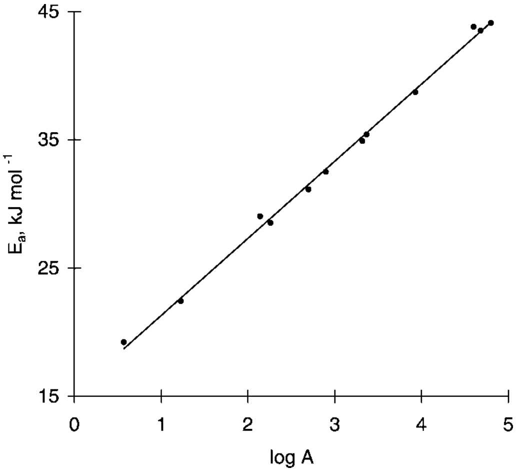

Figure 5. Compensation effect $\{10^4[\mathrm{Cr(VI)}]_0 = 2.0$ g atom dm^{-3}, $10^2[\mathrm{alcohol}]_0 = 5.0$ mol dm^{-3}, $[\mathrm{HClO_4}] = 1.0$ mol dm^{-3}, 30% (v/v) aqueous acetic acid$\}$

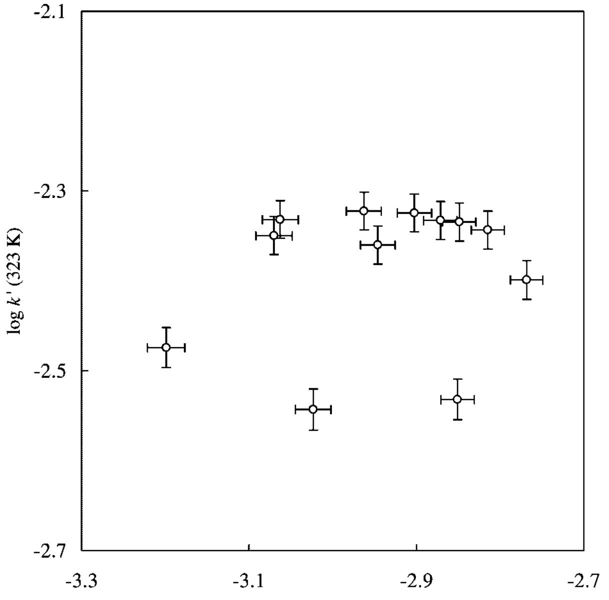

Figure 6. Double logarithmic plot of k' of oxidations of pentan-1-ol with chromium(VI) reagents at 323 and 293 K $\{10^4[\mathrm{Cr(VI)}]_0 = 2.0$ g atom dm^{-3}, $10^2[\mathrm{alcohol}]_0 = 5.0$ mol dm^{-3}, $[\mathrm{HClO_4}] = 1.0$ mol dm^{-3}, 30% (v/v) aqueous acetic acid$\}$

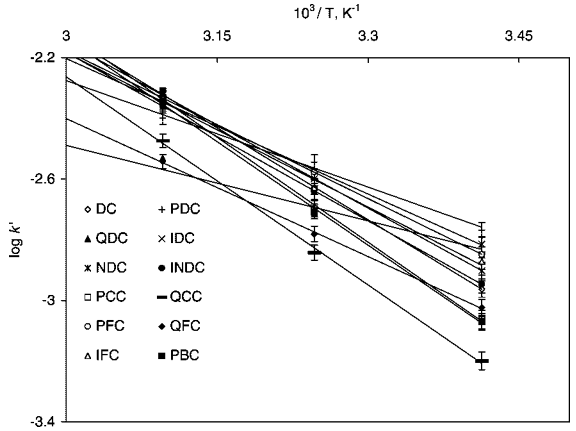

Figure 7. Arrhenius plots for the oxidations of pentan-1-ol with chromium(VI) reagents $\{10^4[\mathrm{Cr(VI)}]_0 = 2.0$ g atom dm^{-3}, $10^2[\mathrm{alcohol}]_0 = 5.0$ mol dm^{-3}, $[\mathrm{HClO_4}] = 1.0$ mol dm^{-3}, 30% (v/v) aqueous acetic acid$\}$

pseudo-first-order conditions $\{10^4[\mathrm{Cr(VI)}]_0 = 2.0$ g atom dm^{-3}, $10^2[\mathrm{alcohol}]_0 = 5.0$ mol dm^{-3}, $[\mathrm{HClO_4}] = 1.0$ mol dm^{-3}, 30% (v/v) aqueous acetic acid$\}$; the rate law is complex and the enthalpies, entropies and free energies of activation were not calculated. Although the activation energy varies linearly with the logarithm of frequency factor (Fig. 5; $r = 0.998$, SD $= 0.487$, slope $= 6.02$ kJ mol^{-1}, number of data sets $n = 12$), the linear relationship between the activation parameters which were calculated from the same data set is statistically incorrect.[25–29] Operation of isokinetic relationship in the oxidation with chromium(VI) reagents could be tested by a linear double logarithmic plot of rates at two temperatures.[25–29] The isokinetic temperature (β) is the temperature at which all the reagents of the series react equally fast; the slope of the double logarithmic plot (b) affords β, $\beta = T_1T_2(b-1)/(bT_2 - T_1)$ where $T_2 > T_1$. The log $k'(T_2)$ − log $k'(T_1)$ relationship in the oxidations of pentan-1-ol with chromium(VI) reagents shows that the QDC, QFC and QCC oxidation rates do not fall in line with others (Fig. 6). The validity of the isokinetic relationship could be found out from the common intersection of the Arrhenius lines. Figure 7 shows the operation of isokinetic relationships, one in the oxidations with DC, PDC, IDC, 3CPDC, 4CPDC, PFC, IFC, PCC and PBC and the other in the oxidations with the quinolinium reagents. The double logarithmic plot of rates at two different temperatures also supports the conclusion. A possible reason for the lack of sharp fit is that the variation of the rate with the reagent is not large ($< 50\%$), and the error in specific rate, as observed in similar kinetic studies, is ±4%. This is because the isokinetic temperature is very close to the experimental temperature. Although some heterocyclics are reported to catalyze chromium(VI) oxidation,[30] this is ruled out in the present study; the oxidation rates of dichromates and halochromates of heterocyclic bases are not significantly larger than that of potassium dichromate. The observed small variation in the oxidation rates among the dichromates is probably due to the association of heterocyclic bases with chromium(VI) species or in the transition state. The common intersection of the Arrhenius lines of the oxidations with chromium(VI) reagents except QDC, QFC and QCC suggests that the involvement of the quinolinium moiety in the transition state is different from that of the other heterocyclic bases.

CONCLUSION

The oxidations of pentan-1-ol with 12 dichromates and halochromates of heterocyclic bases in aqueous acetic acid exhibit identical kinetic behavior. The Arrhenius lines show two common points of intersections, one in the oxidations with DC, PDC, IDC, 3CPDC, 4CPDC, PFC, IFC, PCC and PBC and the other in the oxidations with QDC, QFC and QCC, indicating that the involvement of the quinolinium moiety in the transition state is different from that of the other heterocyclic bases.

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