Oxidation of benzyl alcohol by pyridinium dichromate in acetonitrile. Using the *para/meta* ratio of substituent effects for mechanism elucidation †

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Rate constants were measured for the oxidation reaction of benzyl alcohol and twenty-five *ortho-*, *meta-* and *para-*monosubstituted derivatives in the temperature range 293–323 K at intervals of 10 K. The kinetics were followed spectrophotometrically in dry acetonitrile acidified with trichloroacetic acid (TCA) using pyridinium dichromate (PDC) as oxidising agent under pseudo-first-order conditions with respect to PDC. Benzaldehyde is the only oxidation product and no reaction takes place without TCA. From good linear Eyring plots activation enthalpies $\Delta^{\ddagger}H°$ and entropies $\Delta^{\ddagger}S°$ are calculated. For *ortho-*substituted benzyl alcohols high $\Delta^{\ddagger}H°$ values and small negative $\Delta^{\ddagger}S°$ values point to an *ortho* effect on the rate-determining step. Using the tetralinear approach to substituent effects, the average value $\bar{\lambda} = 1.09 \pm 0.05$ for the *para/meta* ratio of inductive or Electra effects is obtained and negative Hammett reaction constants decreasing in magnitude with increasing temperature are found. A mechanism implicating the prior acid-catalysed formation of neutral benzyl hydrogen dichromate ester followed by intramolecular proton transfer is proposed. Modelling of parameter λ in terms of the electrostatic theory showed its experimental value to be consistent with the ratio of electric potentials generated in the immediate vicinity of the nearest chromium atom by dipolar substituents introduced in the aromatic ring on *para* and *meta* positions. At a molecular level the oxidative, rate-determining step is suggested to be triggered by the retraction or shrinkage of electron pairs from sigma bonds in Cr_2^{VI} species to non-bonding orbitals in unstable Cr^{IV}–O–Cr^{VI} species. In contrast with past interpretations, an electrochemical approach is used to explain negative values for the Hammett reaction constant.

Introduction

Substituent effects on the kinetics of organic reactions in solution are useful tools to probe reaction mechanisms. These tools have recently been applied to study the oxidation of different organic molecules in aqueous[1] and non-aqueous[2] solvents.

An important transformation in organic synthesis is the formation of carbonyl groups using alcohol molecules as starting material.[3] The kinetics of oxidation of benzyl alcohols by various oxidants has also been studied,[1b,4] but not using pyridinium dichromate (PDC) as oxidising agent. The use of PDC as a mild oxidising agent of alcohols in aprotic media was established by Corey and Schmidt.[5] Under these conditions the mechanism for converting primary and secondary alcohols to, respectively, aldehydes and ketones is believed to involve the formation of an ester intermediate.[6] In particular, Sharma and co-workers[6b] gathered compelling kinetic evidence on the formation of an inorganic ester in the oxidation of pentan-2-ol by different chlorochromates, which are chromium(VI) reagents.

Substituent effects can be used to probe the structure of activated complexes. An interesting approach is based on the determination of cross-interaction constants[7] from which distances between substituents in different moieties of activated complexes may be estimated.[8] However, we use a novel method[9] for analysing substituent effects. In the latter method the parameter λ giving *para/meta* ratios[10] of substituent inductive or Electra[11] effects is determined using a constrained tetralinear equation.[12] Experimental λ values are then modelled[9] in terms of the electrostatic theory of substituent effects.

In this work we measure the effect of eight different substituents from *meta*, *para* or *ortho* positions on the oxidation rate of benzyl alcohol with pyridinium dichromate in anhydrous acetonitrile acidified with trichloroacetic acid. We report interesting insights on the mode of interaction between polar substituents and reaction site in these oxidation reactions. We collect evidence showing that (i) this reaction is acid-catalysed, (ii) the oxidative, rate-determining step is a concerted process triggered by the shrinkage of a pair of electrons from a sigma bond into a non-bonding chromium orbital, (iii) this process involves an intramolecular proton transfer in the dichromate ester with formation of benzaldehyde, and (iv) the acceleration effect of dipolar electron-donor substituents from the *meta* and *para* positions is due to increased electric potential

DOI: 10.1039/b200742h

J. Chem. Soc., Perkin Trans. 2, 2002, 1151–1157 **1151**

in the immediate vicinity of chromium atoms undergoing reduction.

Results and discussion

Kinetic analysis

The oxidation of twenty six benzyl alcohols (BnOH) by pyridinium dichromate (PDC) in the presence of trichloroacetic acid (TCA) is studied in acetonitrile at four temperatures in the range 293–323 K. The rate of disappearance of Cr_2^{VI} species is followed spectrophotometrically, from which experimental first-order rate constants k_{obs} are obtained.

Kinetic measurements for establishing rate laws were carried out at 303 K. Rate constants were determined in pseudo-first-order conditions with respect to PDC, using different initial concentrations of PDC, BnOH and TCA. The results from exploratory experiments, which are summarised in Table S1, indicate the reaction to be of first order with respect to each of these reagents. Chemical analysis shows that benzaldehyde is the only product emerging from the oxidation of benzyl alcohol. No reaction is observed in the absence of TCA, pointing to a catalytic action by TCA.

Since direct oxidation of BnOH by PDC is unlikely, on the basis of the above chemical evidence we are led to postulate a mechanism involving the acid-catalysed formation of an ester intermediate. However, to avoid undue complication we beforehand establish which is the main Cr_2^{VI} species formed from the complete dissociation of PDC in acidic acetonitrile solution. The dichromic acid is a diprotic acid of general formula H_2A, its first and second acidity constants being denoted by K_1 and K_2, respectively. Material balance for this acid is expressed by $c_T = [H_2A] + [HA^-] + [A^{2-}]$ so that the fraction of each species is given by $a_0 = [H_2A]/c_T$, $a_1 = [HA^-]/c_T$ and $a_2 = [A^{2-}]/c_T$. Then, in a solution having proton activity h, equilibrium considerations lead to the well-known results in eqn. (1)–(3).
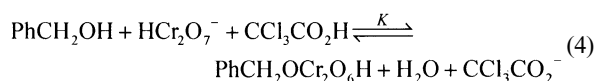
$$a_0 = h^2/(h^2 + K_1h + K_1K_2) \qquad (1)$$

$$a_1 = K_1h/(h^2 + K_1h + K_1K_2) \qquad (2)$$

$$a_2 = K_1K_2/(h^2 + K_1h + K_1K_2) \qquad (3)$$

Using the similar aqueous chromic acid as a rough guide, for which $pK_1 = -0.2$ and $pK_2 = 6.51$ at 25 °C, at a relatively high experimental concentration of trichloroacetic acid (68 mmol dm^{-3}) we estimate that hydrogen dichromate anions account for over 95% of the Cr_2^{VI} species in acetonitrile solution. Therefore, in the mechanistic analysis developed below, the species $HCr_2O_7^-$ is assumed to be the only oxidising agent present in the reacting solution.

For the first step of the oxidation mechanism we take the acid-catalysed formation of the neutral ester intermediate; eqn. (4).

$$PhCH_2OH + HCr_2O_7^- + CCl_3CO_2H \underset{}{\overset{K}{\rightleftharpoons}}$$
$$PhCH_2OCr_2O_6H + H_2O + CCl_3CO_2^- \qquad (4)$$

In the present reacting mixture, no fairly strong external nucleophile can be envisaged in appreciable concentration. Hence, for the second, oxidative step, which is also the rate-determining step, we tentatively propose an intramolecular proton transfer in the dichromate ester, leading to the formation of benzaldehyde and unstable Cr^{IV}–O–Cr^{VI} species; eqn. (5).

$$PhCH_2OCr_2O_6H \overset{k}{\longrightarrow} PhCHO + (H_2Cr_2O_6) \qquad (5)$$
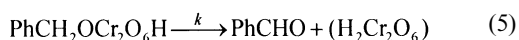
Then the chemical equation for the overall oxidation reaction is given by eqn. (6), which results from summing eqn. (4) and (5).

Eqn. (6) is written in a form that suggests chemical kinetics of first order with respect to PDC, BnOH and TCA, as experimentally found.

$$HCr_2O_7^- + PhCH_2OH + CCl_3CO_2H \longrightarrow$$
$$PhCHO + (H_2Cr_2O_6) + CCl_3CO_2^- + H_2O \qquad (6)$$
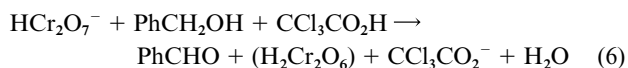
At this stage we observe that no detailed information is available on the structure of the activated complex. In the absence of a firm proposal on the mechanism and since in the kinetic experiments reported here a large excess of substrate over oxidant is used, we calculate experimental second-order rate constants k_2 using eqn. (7), where $[BnOH]_0$ stands for the initially fixed common concentration of each benzyl alcohol in all kinetic runs.

$$k_2 = k_{obs}/[BnOH]_0 \qquad (7)$$

Rate constants and activation parameters

Rate constants k_2 for the present reactions are shown in Table 1, where benzyl alcohols are classified according to the special[10] or normal[14] nature of the ring substituent. As substituents we chose dipolar groups in which the atom linked to the benzene nucleus has a full octet; but only in special substituents does it bear a lone pair of electrons. We note a marked substituent effect on oxidation rates, which are slowed by strong electron-acceptor groups and by any kind of substituent in the *ortho* position.

The kinetic data for each benzyl alcohol are fitted by a least-squares method to the Eyring equation; eqn. (8).

$$\ln(k_2/T) = a + b/T \qquad (8)$$

Good linearity is observed in all cases, individual correlation coefficients being in the range 0.997–1.000. From the regression coefficients in eqn. (8), enthalpies of activation $\Delta^{\ddagger}H°$, entropies of activation $\Delta^{\ddagger}S°$ and their standard deviations are calculated. These quantities are also shown in Table 1, from which is perceived a general trend associating low activation enthalpies with large negative activation entropies. To explore this trend, Exner's plots[15] for the possible verification of an isokinetic relationship (IKR) in the *meta* and *para* series were drawn for the kinetic data in Table 1. The corresponding statistical analysis[16] using the *F*-test failed to corroborate the IKR. Although series of similar reactions sharing a common mechanism usually obey the IKR,[15,16] there are instances in which great structural variation within a given reaction series causes IKR failure.[17] However, changing the substituent in the *meta* or *para* position cannot be regarded as an important structural change. We are thus led to ascribe the poor validation of IKR to the consequences of a complex, multi-step reaction mechanism. Indeed, experimental rate constants k_2 are likely to include contributions from equilibrium quotient K for eqn.(4), which in turn also vary with temperature and substituent. To this end we examine the relation between k in eqn. (5) and k_2 in eqn. (7). Given the meaning of k_{obs}, eqn. (9) is obtained from eqn. (7).

$$k_2 = -\frac{d[Cr_2^{VI}]/dt}{[BnOH]_0[Cr_2^{VI}]} \qquad (9)$$

Since Cr_2^{VI} species are exclusively consumed in the oxidative step [*cf.* eqn. (5)], then eqn. (10) holds and eqn. (11) is also obtained.

$$-d[Cr_2^{VI}]/dt = k[PhCH_2OCr_2O_6H] \qquad (10)$$

$$k = \frac{k_2[BnOH]_0[Cr_2^{VI}]}{[PhCH_2OCr_2O_6H]} \qquad (11)$$

Table 1 Second-order rate constants k_2 at different temperatures, activation enthalpies $\Delta^{\ddagger}H°$ and activation entropies $\Delta^{\ddagger}S°$ for the oxidation of twenty-six benzyl alcohols XPhCH$_2$OH (BnOH) using pyridinium dichromate (PDC) in acetonitrile acidified with trichloroacetic acid (TCA)[a]

| Substituent | $\sigma^{\circ\,b}$ | $k_2/10^{-3}$ dm^3 mol^{-1} s^{-1} | | | | $\Delta^{\ddagger}H°$/kJ mol^{-1} | $-\Delta^{\ddagger}S°$/J K^{-1} mol^{-1} |
		293.15 K	303.15 K	313.15 K	323.15 K		
Special							
m-OMe	0.102	86.7	127	187	280	28.2 ± 0.9	169 ± 3
m-F	0.335	10.3	21.7	46.8	95.1	55.9 ± 1.0	92 ± 3
m-Cl	0.365	11.7	22.7	43.3	83.4	49.0 ± 0.9	115 ± 3
m-Br	0.369	12.7	23.7	43.9	82.3	46.5 ± 1.0	123 ± 3
m-I	0.343	14.0	25.3	45.0	80.0	43.1 ± 0.7	133 ± 2
p-OMe	−0.120	263	367	500	733	24.0 ± 1.3	174 ± 4
p-F	0.151	13.7	24.3	43.3	73.3	41.7 ± 0.4	138 ± 1
p-Cl	0.242	10.3	20.7	40.0	76.7	49.9 ± 0.5	113 ± 2
p-Br	0.265	11.0	19.4	37.2	73.3	47.3 ± 2.4	121 ± 8
p-I	0.277	26.0	41.7	63.3	98.4	32.2 ± 0.5	165 ± 2
o-OMe	—	50.0	100	190	420	52.7 ± 2.6	90 ± 8
o-F	—	7.50	19.0	41.0	100	64.7 ± 1.8	65 ± 6
o-Cl	—	6.20	16.0	38.0	88.0	66.9 ± 0.3	59 ± 1
o-Br	—	5.90	14.0	36.0	79.0	66.2 ± 1.4	62 ± 5
o-I	—	7.00	18.0	40.0	94.0	65.1 ± 1.1	64 ± 4
Normal							
H	0	70.7	125	273	497	49.6 ± 2.6	98 ± 9
m-Me	−0.062	107	146	201	274	22.2 ± 0.4	188 ± 1
m-CO$_2$H	0.356	12.7	22.6	40.0	76.7	44.4 ± 1.9	130 ± 6
m-NO$_2$	0.713	0.225	0.697	2.17	6.37	85.3 ± 1.2	24 ± 4
p-Me	−0.135	113	167	237	367	27.9 ± 1.4	168 ± 5
p-CO$_2$H	0.440	3.67	8.33	18.0	43.3	61.8 ± 2.2	81 ± 7
p-NO$_2$	0.814	0.150	0.380	1.06	3.28	78.3 ± 4.1	52 ± 13
o-Me	—	43.0	88.4	180	370	53.9 ± 1.1	87 ± 4
o-Et	—	37.0	78.0	170	340	56.0 ± 0.9	81 ± 3
o-CO$_2$H	—	2.80	6.30	15.0	39.0	66.4 ± 3.2	68 ± 10
o-NO$_2$	—	0.140	0.350	1.20	2.78	77.7 ± 4.0	54 ± 13

[a] [BnOH]$_0$ = 30 mmol dm^{-3}, [PDC]$_0$ = 1.0 mmol dm^{-3} and [TCA]$_0$ = 68 mmol dm^{-3}. [b] Unified sigma-zero substituent constants taken from ref. 13.

Next we define quotient $Q = [CCl_3CO_2^-]/[CCl_3CO_2H]$, which is a constant at fixed temperature. In these terms from the equilibrium quotient K for eqn. (4) follows an expression for the ester concentration; eqn. (12).

$$[PhCH_2OCr_2O_6H] = \frac{K}{Q} \cdot \frac{[BnOH][HCr_2O_7^-]}{[H_2O]} \qquad (12)$$

From stoichiometric analysis it is clear that $[H_2O] = [BnOH]_0 - [BnOH]$, and from our initial simplifying assumption it is also clear that $[Cr^{VI}] = [PhCH_2OCr_2O_6H] + [HCr_2O_7^-]$. Hence combining these results with eqn. (11) and (12) yields the interesting equation, eqn. (13).

$$k = k_2[BnOH]_0 \left(1 + \frac{Q}{K} \left(\frac{[BnOH]_0}{[BnOH]} - 1 \right) \right) \qquad (13)$$

This equation nicely shows that k_2 is not a pure rate constant. Indeed, it contains contributions from the temperature dependent quantity Q and from the temperature and substituent dependent quantity K. On the other hand, it is also true that in kinetic experiments under pseudo-first-order conditions with respect to PDC the last term in eqn. (13) becomes close to zero. Under these circumstances the pure first-order rate constant k for the oxidative step is approximately proportional to the measured k_2, the proportionality constant being then independent of the substituent nature.

We turn attention to the analysis of activation enthalpies in the *ortho* series (Table 1). Except for the nitro group, in each of the other seven cases the highest activation enthalpy is associated with *ortho* substitution. Since the chemistry of the nitro group as a substituent is reviewed by Exner and Krygowski,[18] we do not discuss this substituent further. The trend noted above for activation enthalpies is normally regarded as supporting evidence for a bimolecular rate-determining step in which the attack on the substrate is sterically hindered. However, on close inspection we observe that these activation enthalpies span over a small range of energy values. Most noteworthy are the values for the halogen family, which are almost insensitive to the wide difference in size of their elements. No doubt the *ortho* substitution will entail a less energetically favourable route to be followed, but will still be consistent with the proposed unimolecular decomposition of the ester in the oxidative step.

Analysis of *meta* and *para* substituent effects

Preliminary analysis of rate constants in Table 1 revealed that substituent effects in the *meta* and *para* series are best described using $\sigma°$ constants. The suggestion is that in activated complexes the reaction centre be effectively insulated against through-resonance interactions from substituents.

We apply the constrained tetralinear approach[12] to substituent effects in benzene derivatives. In the correlation analysis of a given reaction series, this method uses four regression straight lines, each assigned to one of the following subsets: *meta* normal, *para* normal, *meta* special and *para* special substituents. We note that a total of eight independent parameters would be required for an unconstrained fit of the data. However, the use of a hyperbolic model for the *meta–para* interrelationship[10] has allowed reduction of the number of adjustable parameters to four in the case of the Hammett equation[12a] and to five in the case of the Yukawa–Tsuno equation.[12b] In the context of the tetralinear method reaction series are conveniently described using the parameters λ and γ. The former yields experimental values for the *para/meta* ratio of the substituent inductive or non-mesomeric effect, which has been proposed[9,11] to be named the Electra effect. The parameter γ is a sort of absolute Hammett reaction constant.[12] The observation is made that the present analysis is based on a large number of different substituents distributed over the four

Table 2 Tetralinear analysis of the oxidation rates of *meta* and *para* monosubstituted benzyl alcohols in acetonitrile at different temperatures[a]

| Parameter | Temperature/K | | | |
	293.15	303.15	313.15	323.15
λ	1.10 ± 0.14	1.12 ± 0.14	1.09 ± 0.13	1.05 ± 0.17
γ	0.62 ± 0.15	0.58 ± 0.09	0.55 ± 0.08	0.51 ± 0.09
$\gamma/\gamma°$	-2.76	-2.56	-2.45	-2.25
s^{b}	0.28	0.25	0.27	0.29

[a] Data from Table 1 in the form $\log (k_{2,X}/k_{2,H})$ fitted to the constrained tetralinear equation[12] using $\sigma°$ constants.[13] [b] Standard deviation of the fit.

subsets described above. Indeed, this is the cost for obtaining reliable experimental estimates of parameters λ and γ.

Using a previously described non-linear least-squares computing program,[12] values of $\log (k_{2,X}/k_{2,H})$ are correlated with $\sigma°$ substituent constants[13] in terms of the constrained tetralinear equation.[12] This equation, in the version with four fitting parameters, yields the values shown in Table 2, the associated standard deviations being given by a Monte Carlo procedure.[9,12b]

For the reference ionisation process in solution used to build the $\sigma°$ scale,[10] $\gamma° = -0.225$. Therefore, in the framework of the tetralinear approach $\gamma/\gamma°$ is the equivalent of Hammett reaction constant ρ.[12] From Table 2 we observe that the negative $\gamma/\gamma°$ decreases in magnitude with increasing temperature.

Parameter λ and mechanism

The Electra effect does not depend on temperature, at least over a modest range of 40 K. Likewise no temperature effect on experimental λ values can be inferred from Table 2. Hence our discussion will be based on the average value for the experimental *para/meta* ratio of the Electra substituent effect, which is found to be $\bar{\lambda} = 1.09 \pm 0.05$.

The parameter λ has been successfully modelled[9,12] in terms of the electrostatic theory. Here we use this modelling in an attempt to elucidate the activated complex (AC) structure, which is the key to the characterisation of the reaction mechanism.

Substituent effects on reaction rates measure the changes operated at molecular level on going from the ground state to AC along the oxidative pathway. We are faced with the task of finding the AC structure and mode of action for dipolar substituent effects that are simultaneously compatible with the relatively high average value of 1.09 for the parameter λ. Using a recent accurate procedure,[9] we performed systematic calculations in order to model the value $\bar{\lambda} = 1.09$ for the benzyl hydrogen dichromate molecule. We started with the case of a dipolar reaction site being 0.1 nm in length and being localised along the phenyl 1,4 axis. If that λ value were for dipole–dipole interactions, then the reaction-centre middle-point would be 0.72 nm from the aromatic ring (Fig. 1), which is unrealistic.
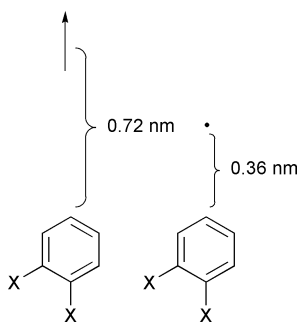

Fig. 1 Models for dipole–dipole and dipole–charge interactions in benzene derivatives yielding $\lambda = 1.09$.

Indeed, this would lie on the outskirts of the ester molecule. Further, this distance increases with increasing length of the dipolar reaction centre as well as for most other angular orientations. Next we examined the case of dipole–charge interactions. We found that the value of 1.09 for the *para/meta* ratio of electrostatic interaction energies is obtained when an electric charge is placed at 0.36 nm from the aromatic ring on its 1,4 axis (Fig. 1). In this case the calculated distance is encouraging because it corresponds to the immediate vicinity of the chromium atom undergoing reduction. However, it also poses the embarrassing question of the origin and sign of that charge. To find the way out of this dilemma we need to break with common wisdom. We refer here to the well-established theory of polar effects on the rates of reactions for which the transition state formation is accompanied by great redistribution of electric charges.

Now we are dealing with a redox process in which a transition element changes its oxidation state. Therefore, by drawing an analogy with the influence of the electric potential on the rates of electrode reactions,[19] we can develop a different interpretation of polar effects. To this end we return to basic electrostatic theory[9] and note that the electric potential V created at a given point by a dipole composed of symmetrical charges is the sum of the potentials originated separately by the charges Q and $-Q$, being described by eqn. (14).

$$V = \frac{Q}{4\pi\varepsilon} \left(\frac{1}{r_+} - \frac{1}{r_-} \right) \qquad (14)$$

In this equation ε is the medium electric permittivity and the interaction distances r_+ and r_- refer to the corresponding point charges in the dipole. In these terms the ratio of electric potentials generated by a given substituent from the *para* and from the *meta* positions is expressed by eqn. (15).

$$\lambda_e = \frac{V_p}{V_m} = \left(\frac{1}{r_+} - \frac{1}{r_-} \right)_{para} \bigg/ \left(\frac{1}{r_+} - \frac{1}{r_-} \right)_{meta} \qquad (15)$$

Most appropriately, in the context of actions mediated by changes in the electric potential we have arrived at a theoretical expression for the parameter λ which is exactly the same as that holding in the case of dipole–charge interactions.[9] This illuminating result puts us again on the right path.

In line with previous research on the ester mechanism for similar oxidation reactions,[4e,20,21] we favour the formation of planar five-member cyclic ground and transition states stabilised by intramolecular hydrogen bonds linking an oxygen atom from the inorganic moiety to an α-hydrogen in the organic counterpart (Fig. 2). Using structural data for the molecular
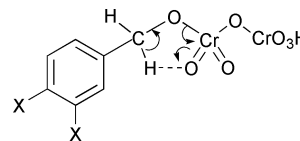

Fig. 2 Proposed cyclic transition state in the oxidation of benzyl alcohols by hydrogen dichromate ions.

ester (see Experimental section), in the corresponding ground state the hydrogen bond CH $\cdots$ O=Cr is estimated to be 0.20 nm in length, which is typical for weak hydrogen bonds[22] and is to be compared with the value 0.185 nm in pure liquid water. For this molecular framework we assume free rotation about the C–C single bond. Then in relation to the aromatic ring 1,4 axis the nearest chromium atom describes a circle on a plane 0.234 nm distant from the ring, as depicted in Fig. 3. The circle radius is calculated to be 0.225 nm. Because the theoretical parameter λ depends on the rotational angle ϕ in the ester, we

use a previously described procedure[9] to estimate an average $\bar{\lambda}_e(\phi)$ value; eqn. (16).

$$\bar{\lambda}_e(\phi) = \int_0^{2\pi} \lambda_e(\phi)\mathrm{d}\phi/2\pi \qquad (16)$$

Individual λ_e values are calculated at different rotations ϕ by inserting analytically determined distances in eqn. (15). These values, which range from 0.995 to 1.452, lead to the smooth curve shown in Fig. 4. Their numerical integration yields the
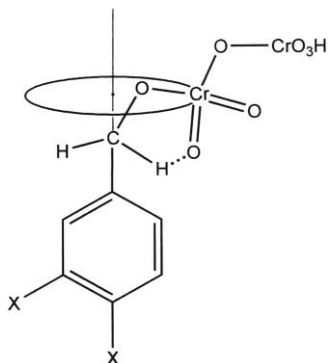

Fig. 3 In molecules of benzyl hydrogen dichromate, changing conformation will affect interaction distances from *meta* and *para* substituents to the nearest chromium atom.
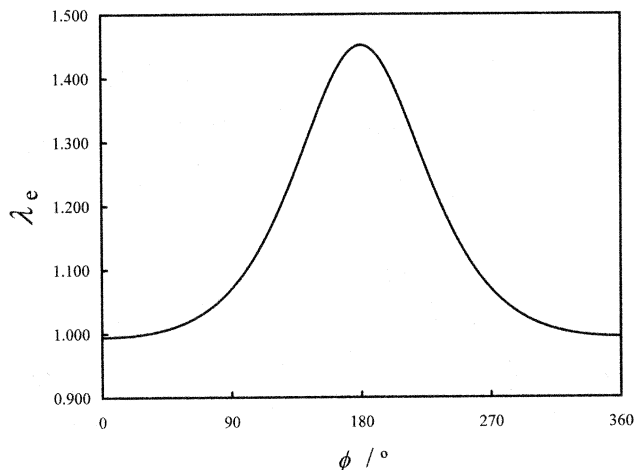

Fig. 4 The *para/meta* ratio of electric potential effects on the nearest chromium atom, λ_e, for dipolar substituents in the cyclic ester benzyl hydrogen dichromate (see Fig. 3) as a function of the rotation ϕ about the benzene nucleus 1,4 axis.

average value $\bar{\lambda}_e(\phi) = 1.139$. In another modelling experiment, the reaction centre was displaced to the O–Cr ester-bond middle point. For this geometry the circle (radius, 0.187 nm) lies on a plane at a distance of 0.218 nm, the individual $\lambda_e(\phi)$ values are in the range 1.001–1.173 and the average value $\bar{\lambda}_e(\phi) = 1.058$ is obtained. Rather suitably, the experimental average value of 1.09 for the parameter λ is between these marks.

Therefore, from the modelling of *para/meta* ratios for substituent Electra effects on rate constants we have confirmed the formation of an ester intermediate. More importantly, we obtain strong evidence supporting the view that the rate of this oxidation reaction is influenced by changes in the electric potential in the vicinity of the chromium atom to be reduced.

Parameter γ and substituent effect

We still need to conciliate the observed negative γ/γ° values (Table 2) with the likely absence of positive charge development in the transition state.

The meaning of negative values for the Hammett reaction constant in oxidation reactions has been a difficult matter.[21]

Negative reaction constants are traditionally associated with an electron-deficient centre in transition states; a convention originally developed from the analysis of substituent effects in nucleophilic displacement reactions. Negative reaction constants have been used by Banerji[4a,f,g,23] as supporting evidence for oxidation mechanisms involving a hydride-ion transfer in the rate-determining step. It has also been linked to the oxidative formation of a carbonyl group, which would seemingly be favoured by electron-donating substituents.[4f,21] Next we develop further our electrochemical approach to explain the acceleration effect of *meta* and *para* electron-donor substituents on the rates of oxidation reactions occurring by the ester mechanism. We need, however, to clarify the electronic structure of the ester. For dichromate compounds we did not find evidence supporting an octahedral structure around chromium atoms, and hence the d^2sp^3 hybridisation state in the latter, as assumed by Kwart and Nickle[24] for chromate esters. Instead, oxochromium compounds should have a tetrahedral structure resulting from the sp^3 hybridisation state in chromium atoms. In addition to forming four sigma bonds, this state leaves two unpaired d electrons for establishing d–p pi bonds with two oxygen atoms. We conclude that one sp^3 chromium orbital is engaged in the O–Cr sigma bond being broken in the oxidative step.

Then the actual redox process in dichromate ester molecules is triggered by the two electrons in the O–Cr sigma bond retracting into a non-bonding sp^3 orbital in chromium atoms. In this process there is a change in oxidation state from VI to IV, together with the corresponding loss of valence, but the hybridisation state of chromium atoms remains sp^3. According to our approach, reactions initiated by the shrinkage of electron pairs are promoted by increasing the electric potential on the sigma bonds to be broken. Conversely, the electric potential lowering due to electron-acceptor substituents in the organic moiety will slow down the valence loss in the atom being reduced and hence the oxidation rate. Therefore, the Electra effect on these oxidation rates seems to be primarily an effect on the ground state, rather than on the transition state. The mode of substituent action described above entails the observation of negative Hammett reaction constants, in agreement with experimental evidence. Further support for this interpretation is obtained from electrode kinetics. Thus the reduction of substituted benzaldehydes on a mercury electrode is faster the more electron accepting the substituent.[25] However, our proposal represents a break with conventional interpretations that simply extend to redox reactions the concepts of charge stabilisation and destabilisation in transition states, the former leading to increased reaction rates and the converse for the latter.

Another controversial aspect is related to the electron flow in electrocyclic mechanisms for the unimolecular decomposition of the ester.[4a,e,6b,20,21,23,24] Stewart and Lee[21] refer to this problem as a vexing question. We can now offer a clear answer (see Fig. 2). If the retraction of sigma electrons towards chromium atoms initiates the electron flow, then the ensuing electron movements are clarified. Thus, electrons forming the d–p pi bond retract to the oxygen atom engaged in the hydrogen bond, which in turn becomes a covalent bond. Ultimately, the electrons liberated by this proton transfer are used to form the carbonyl pi bond. We comment that the only long undisputed feature in ester mechanisms has been the heterolysis of the C–H bond.[26]

Activation parameters and mechanism

In the cases of *meta* and *para* monosubstituted benzyl alcohols, we note from Table 1 that low activation enthalpies are associated with electron-donating substituents which raise the electric potential on the reaction site. Then the extent of bond breaking should be small and earlier transition states are formed. If so, incipient bond polarisation in the internal cyclic structure would account for a lesser degree in the loss of solvation

entropy and thus for smaller negative activation entropies, as experimentally found (Table 1). In a similar manner, electric-potential lowering substituents raise enthalpic activation barriers, late transition states are formed, and more significant bond polarisation and entropy loss due to extra solvation occur.

It remains to conciliate a unimolecular rate-determining step with the observed *ortho* retarding effect, which arises from the conjunction of high activation enthalpies with small negative activation entropies. In ground and transition states stabilised by intramolecular hydrogen bonds, the *ortho* substitution sterically hinders the free rotation of internal cycles in ester molecules and activated complexes. This hindrance has been confirmed using space-filling molecular models. Since rotation between certain angles will jeopardise stabilisation by intramolecular bonding, *ortho* derivatives are destabilised. Interestingly, this unusual *ortho* effect is only slightly dependent on the substituent bulkiness. Its effect on activation entropies will be common to each substituent. Excluding the anomalous nitro group, for the other seven different substituents the loss in activation entropy amounts, on average, to 46% when a given group is moved from either *para* or *meta* positions to the *ortho* position. We attribute low entropy losses on activation to diminished solvation of both ground and transition states resulting from bulky *ortho* groups.

Concluding remarks

In summary, from the analysis of chemical data for oxidation rates of benzyl alcohol (BnOH) using pyridinium dichromate (PDC) in acetonitrile solution acidified with trichloroacetic acid (TCA), we have gathered evidence that strongly supports the following detailed mechanism proposal.

(i) The main oxidising species are hydrogen dichromate ions ($HCr_2O_7^-$), the kinetics being first order with respect to $HCr_2O_7^-$ (as a representative for PDC), BnOH and TCA.

(ii) TCA is a catalyst in the formation of intermediate benzyl hydrogen dichromate molecules, which are stabilised by intramolecular hydrogen bonds.

(iii) The oxidative, rate-determining step is initiated by the change in oxidation state from VI to IV taking place in chromium atoms. During this reduction chromium sp^3 orbitals engage incoming electron pairs from O–Cr sigma bonds. In the ensuing electron cyclic transfer, heterolysis of Cr=O d–p pi bonds occurs, protons are transferred along hydrogen bonds from carbon to oxygen atoms, and disengaged electrons in carbon atoms are used to form the new carbonyl pi bond from which benzaldehyde molecules are produced. Chemical bonds across the five-member cyclic transition states are expected to show varying polarity differences.

(iv) Oxidation rates are increased by *meta* and *para* electron-donor substituents because these polar groups increase the electric potential near chromium atoms, thus facilitating their reduction in oxidation state. Since the converse mode of action applies to electron-acceptor substituents, this mechanism proposal is consistent with the experimentally observed negative Hammett reaction constants.

(v) Oxidation rates are slowed by both electron-donor and electron-acceptor substituents in the *ortho* position. This retarding effect is ascribed to bulky groups, which partially hinder the stabilising formation of intramolecular hydrogen bonds in the ester and cause steric inhibition of solvation.

Experimental

Materials

Pyridinium dichromate was prepared as described in ref. 5. All benzyl alcohols (Fluka) were high-purity chemicals and used as received. The remaining chemicals were of analytical reagent grade. The solvent acetonitrile was subjected to an efficient dry-ing procedure by being repeatedly distilled over phosphorous pentaoxide (P_2O_5) until the drying agent no longer became coloured. To remove traces of P_2O_5, the dried acetonitrile was distilled over anhydrous potassium carbonate followed by distillation without a drying agent.

Kinetic measurements

All kinetic runs were carried out in glass stoppered iodine flasks protected from light. The temperature was kept constant to within ±0.01 K. Unless otherwise stated, reacting solutions prepared with 1.0, 30 and 68 mmol dm^{-3} of, respectively, pyridinium dichromate (PDC), monosubstituted benzyl alcohol and trichloroacetic acid in acetonitrile were sampled at different time intervals. The rate of disappearance of PDC under pseudo-first-order conditions was followed spectro-photometrically by monitoring the decrease in absorption of PDC at 350 nm employing a JASCO UDIVEC 340 UV-V spectrophotometer fitted with variable temperature control.

In terms of the Beer–Lambert law, measured absorbances A_t are directly proportional to concentrations in Cr_2^{VI} species. Experimental first-order rate constants k_{obs} were calculated from the negative slope of linear plots of ln A_t *vs.* time. Duplicate kinetic runs were made in every case. Reported rate constants are reproducible to within ±4%.

Product analysis

After at least 70% conversion, reaction mixtures from actual kinetic runs for benzyl alcohol and each of their twenty-five monosubstituted derivatives were neutralised with sodium hydrogen carbonate and extracted with chloroform. Using IR and UV spectrophotometers, analysis of the extracts showed the presence of benzaldehyde or the corresponding X-substituted derivative. Analysis by TLC and HPLC confirmed the formation of aldehydes in quantitative yield and did not detect the presence of corresponding carboxylic acids. Finally, semicarbazones of the produced aldehydes were prepared and isolated, their melting points being determined.

Structural data

In X-substituted benzyl hydrogen dichromate molecules, the average interatomic distance C–X was taken to be [12a] 0.153 nm. All the other distances (nm) and angles ϕ (°) are from Sutton's tables,[27] as follows: C–C (benzene), 0.139; C_1–C_2, 0.152; C_1–H, 0.109; C_1–O, 0.147; O–Cr, 0.177; Cr=O, 0.163; ϕ (benzene ring), 120; ϕ (tetrahedral carbon and chromium atoms), 109.5; ϕ (C–O–Cr), 112; ϕ (Cr–O–Cr), 115.

Acknowledgements

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