Potassium hydrogen sulfate mediated kinetics and mechanism of oxidation of certain polyols by Quinolinium bound Cr(VI) reagents

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Abstract

Potassium hydrogen sulfate (KHSO_4) mediated oxidation of certain alcohols (Polyols) has been studied by quinolinium bound Cr(VI) reagents like quinolinium dichromate (QDC) and quinolinium chlorochromate (QCC) at different temperatures. Reaction kinetics revealed second order kinetics with a first order in [Alcohol] and [Cr(VI) reagent] at constant bisulfate concentration. Ten fold variation of added [KHSO_4] enhanced the observed rateconstant (k') by ten fold, showing first order dependence on [KHSO_4]. Most plausible mechanisms for QDC oxidation and QCC oxidation of polyols are proposed on the basis of observed kinetic features.

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Graphic abstract

Keywords Quinolinium dichromate (QDC) · Quinolinium chlorochromate (QCC) · Oxidation of certain sugar alcohols · Bisulfate medium · Kinetics · Mechanism

1 Introduction

Acid dichromate ($H_2Cr_2O_7$), and acid chromate ($HCrO_4$) are among the most important hypervalent chromium $[Cr(VI)]$ reagents [1–4], which received the attention of organic and analytical chemists due to their striking oxidizing capability. But, several environmental issues triggered when unspent $Cr(VI)$ solutions were sent through the industrial and laboratory outlets. Moreover, $Cr(VI)$ is toxic in nature.

Besides, over oxidation occurred in many cases when acid dichromate ($H_2Cr_2O_7$) and/or acid chromate ($HCrO_4$) are used as reagents in organic synthesis. These issues became stimulus to synthesize modified hexavalent chromium $Cr(VI)$ reagents [5–14]. As a result, several new and selective $Cr(VI)$ dichromates and halochromates comprising heterocyclic base were synthesized and explored as oxidizing agents [5–20] in organic synthesis. Karunakaran research group at Annamalai University [19, 20] explored

comparative kinetic and mechanistic features related to the oxidation of certain primary alcohols and dimethyl sulfide by several dichromates and halochromates. Over the years, traditionally available Brønsted acids, such as HF, HCl, HBr, HClO_4 , H_2SO_4 , and several carboxylic acids (R-COOH) like CH_3COOH , CH_2ClCOOH , CHCl_2COOH , CCl_3COOH , and CF_3COOH were explored as homogeneous catalysts in organic synthesis, kinetics and mechanism. But due care is necessary when handling these acids as feedstock in chemical laboratories' and industries. Some of them also trigger environmental pollution when they are sent through laboratory and industrial outlets [21, 22].

Potassium bisulfate or potassium hydrogen sulfate (KHSO_4) is a potassium salt of sulfuric acid (H_2SO_4) which is widely used as a household preservative additive in food stuffs because it prevents the growth of harmful bacteria, fungi, and insects which spoil the quality of food. It is also widely used as leavening agent in the preparation of cakes. At the same time it received remarkable attention as an efficient catalyst in several homogeneous and heterogeneous reactions [23–31]. Its catalytic activity is mainly attributed to the in situ generation of (H^+) ions due to the dissociation bisulfate ion (HSO_4^-). Recent reviews published by Ponra et al. [31] and Bitra Baghernejad [32] provide an excellent bibliography on the use of KHSO_4 as an inexpensive, ecofriendly, highly reactive, easy to handle and non-toxic catalyst for various organic transformations, affording the corresponding products in excellent yields with high selectivity catalyst.

erythritol, xylitol, sorbitol, and mannitol) using QDC and QCC in aqueous KHSO_4 media.

2 Experimental

2.1 General

Alcohols, and KHSO_4 were obtained from Avra (India), and Sigma-Aldrich (India) and used as received from the local vendor. Infra Red spectra were recorded on Perkin-Elmer infrared spectrometer, and NMR spectra on a Bruker Avance 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) in $\text{DMSO}-d_6$ with tetramethylsilane (TMS) as an internal standard. TLC experiments were performed on Merck TLC Silica gel 60 F_{254} plates eluting with EtOAc and developed with iodine. Melting points were determined in glass capillaries on a Mel-Temp 3.0.

Quinolinium dichromate (QDC) and quinolinium chlorochromate (QCC) were prepared according to literature procedures as described [14, 15]. For the synthesis of quinolinium dichromate (QDC), 86 ml of quinoline have been added in small portions to the aqueous solution of CrO_3 (100 g/100 ml), with constant stirring. The solution has been diluted to 400 ml with acetone and the contents are cooled up to -20°C . An orange colour QDC solid separated out. The solid has been washed with acetone and the dried sample is recrystallised from water. On the other

Chart-I: Structures of different alcohols

Encouraged by the foregoing literature survey on halochromates, dichromates, and importance of mild and eco-friendly bisulfate catalyst, we have taken up a detailed kinetic study of selective oxidation of sugar alcohols (poly alcohols viz., ethylene glycol(EG), glycerol,

hand, quinolinium chlorochromate (QCC) has been prepared by the method of Singh et al. [16] which is almost similar to the preparation of QDC, except for using 6 M hydrochloric acid instead of water. About 86 ml of quinoline have been added in small portions to the acidic CrO_3 (100 g/100 ml) solution (dissolved in aqueous hydrochloric

acid (6 M) solution) of with constant stirring for 15–20 min under chilled conditions (at 0 °C). This afforded an orange solid, which was filtered in a sintered glass funnel, dried for about an hour (1 h) in vacuum. Purity of the QDC and QCC reagents is checked by elemental analysis, infrared spectroscopic analysis [33], and by standard iodometric procedures [34].

2.2 Kinetic studies

Progress of the QXC—alcohol reactions (where QXC = QDC or DCC) were monitored spectrophotometrically using a double beam Shimadzu UV–visible spectro photometer equipped with thermostatic cell compartment. Recorded absorbance (A) values are proportional to the unreacted [QXC], which were reproducible with in $\pm 5\%$ error limits.

2.3 Stoichiometry and products of oxidation

Stoichiometry of the QXC–ROH (where QXC = QCC or QDC; and ROH = alcohol) reactions was determined under the conditions of [QXC] slightly excess over [ROH] in aqueous bisulfate medium, and absorbance of the [QXC] was recorded periodically till the reaction is completed. From the change in absorbance values of [QXC], it was found that one mole of [QXC] oxidized one mole of alcohol (ROH). In a typical experiment, ROH (0.05 mol) and QXC (2.37 g, 0.01 mol) were made up to 50 cm³ in aqueous bisulfate medium, and kept in the dark for about 15–20 h to ensure completion of the reaction. After completion of the reaction, as ascertained by TLC, the reaction mixture was treated with dichloro methane (DCM) or pet ether. Organic layer was separated and the solvent evaporated to get the final product. The QXC–ROH reaction afforded carbonyl compound (corresponding aldehyde) as the oxidation product by spectroscopic methods.

2.4 Spectroscopic data of products

Acetaldehyde: bp: 21 °C (Obtained 21–22 °C); IR Vmax; 3410, 2995, 1732, 1415, 1355, 952, 758; ¹H NMR (CDCl₃): 2.16 (d, 3H, CH₃), 9.65 (t, 1H, CHO); ¹³C NMR (CDCl₃): 3.60, 199.7; LCMS Mass: 44.

2-hydroxyacetaldehyde (Glycolaldehyde): mp: 97 °C (Obtained 95–96 °C); IR Vmax; 3535, 2875, 1738, 1415, 1102, 852, 745; ¹H NMR (CDCl₃): 3.52 (d, 3H, CH₂), 5.39 (d, 1H, CH₂), 6.27 (d, 1H, OH), 6.82 (d, 1H, CHO in the form of OH); ¹³C NMR (CDCl₃): 66.52, 90.50; LCMS Mass: 120.

Glyceraldehyde: mp: 145 °C (Obtained 143–144 °C); IR Vmax; 3385, 2972, 1650, 1565, 867; ¹H NMR (CDCl₃): 4.10 and 3.78 (t, 2H, CH₂), 4.36 (t, 1H), 4.88 (s, 1H), 6.08 (s, 1H), 9.54 (d, 1H, CHO); ¹³C NMR (CDCl₃): 91.5, 79.5, 60.2; LCMS Mass: 90.

(2R,3S,4R)-2,3,4,5-tetrahydroxypentanal (D-Ribose): mp: 98.5 °C (Obtained 97–98 °C); IR Vmax; 1345, 1315, 1282, 878, 625; ¹H NMR (CDCl₃): 3.47 (t, 1H), 3.52–3.57 (t, 2H), 3.68 (t, 1H), 3.88 (s, 1H, 5-OH), 4.35 (s, 2H, 3 & 4-OH), 4.34 (t, 1H), 5.12 (s, 2-OH), 9.45 (d, 1H, CHO); ¹³C NMR (CDCl₃): 95.02, 70.90, 70.1, 68.2, 64.1; LCMS Mass: 150.

(2R,3R,4S,5S)-2,3,4,5,6-pentahydroxyhexanal (L-Altrose): mp: 107–109 °C (Obtained 107–108 °C); IR Vmax; 3382, 2914, 2852, 1445, 1030; ¹H NMR (CDCl₃): 3.42–3.54 (m, 4H), 3.87 (s, 1H, 6-OH), 4.31 (t, 1H, 2-OH), 4.42 (s, 2H, 3,5-OH), 4.43 (s, 1H, 4-OH), 5.03 (s, 1H, 2-OH), 9.54 (d, 1H, CHO); ¹³C NMR (CDCl₃): 198.2, 88.1, 71.1, 70.1, 68.5, 63.9; LCMS Mass: 180.

(2S,3R,4S,5S)-2,3,4,5,6-pentahydroxyhexanal (D-Glucose): mp: 150–152 °C (Obtained 151–152 °C); IR Vmax; 3392, 3193, 2944, 1437, 1349, 1014, 992, 610; ¹H NMR (CDCl₃): 3.39–3.48 (m, 4H), 3.82 (s, 1H, –OH), 4.28 (t, 1H, 2-OH), 4.39 (s, 2H, 3,5-OH), 4.41 (s, 1H, 4-OH), 5.01 (s, 1H, 2-OH), 9.50 (d, 1H, CHO); ¹³C NMR (CDCl₃): 197.1, 87.1, 70.1, 69.5, 67.4, 62.8; LCMS Mass: 180.

The product analysis was also carried out under kinetic conditions. The solution was then treated with an excess (200 cm³) of a saturated solution of Brady's reagent (2,4-dinitrophenylhydrazine) in 2 mol/dm³ acid and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenyl hydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP derivative was found to be in 75–80% range. Melting points of the 2,4-DNP derivatives were determined which were found to agree well with literature reports [34–39].

In addition to the Brady's 2,4-DNP test, the isolated carbonyl product was further treated with 3,5-dinitrosalicylic acid (DNSA) reagent, with a view to confirm the presence of free carbonyl group (>C=O) in the reducing sugars. The aldehyde group present in the reduced DNSA to 3-amino 5-nitrosalicylic acid (ANSA), while the aldehyde group is oxidised to corresponding acid. The ANSA thus formed a reddish brown complex under alkaline conditions which indicated absorption maximum at 540 nm [39–43].

Fig. 1 Plot of $\ln(A_0/A)$ versus Time at 303 K in QXC oxidation of Ethyleneglycol. [Ethyleneglycol] = 0.333 mol/dm³; [KHSO₄] = 0.167 mol/dm³; 10⁴[QDC] = 1.33 mol/dm³

Fig. 2 Plot of $\ln(A_0/A_t)$ versus Time at 303 K in QXC oxidation of Glycerol. [Glycerol] = 0.333 mol/dm³; [KHSO₄] = 0.167 mol/dm³; 10⁴[QDC] = 1.33 mol/dm³

Fig. 3 Plot of $\ln(A_0/A_t)$ versus Time at 303 K in QDC oxidation of Erythritol. [Erythritol] = 0.333 mol/dm³; [KHSO₄] = 0.167 mol/dm³; 10⁴[QDC] = 1.33 mol/dm³

Fig. 4 Plot of $\ln(A_0/A_t)$ versus Time at 303 K in QDC oxidation of Mannitol. [Mannitol] = 0.167 mol/dm³; [KHSO₄] = 0.167 mol/dm³; 10⁴[QDC] = 1.33 mol/dm³

2.5 Test for free radicals

In order to gain an insight into the mode of electron transfer in the oxidation mechanism, we have tried to detect the nature of intermediates by the addition of olefinic monomer (acryl amide and acrylonitrile in separately) to

Fig. 5 Plot of $(10^4 k')$ versus [ROH] in QCC reactions at 303 K. [KHSO₄] = 0.167 mol/dm³; 10⁴[QDC] = 1.33 mol/dm³

Fig. 6 Plot of $(10^4 k')$ versus [ROH] in QCC reactions at 303 K. [KHSO₄] = 0.167 mol/dm³; 10⁴[QDC] = 1.33 mol/dm³

Fig. 7 Plot of $(10^4 k')$ versus [ROH] in QDC reactions at 303 K. [KHSO₄] = 0.167 mol/dm³; 10⁴[QDC] = 1.33 mol/dm³

the reaction mixture under nitrogen atmosphere. But the added olefinic monomer did not afford vinyl polymer even under elevated temperatures and inert atmosphere. This observation revealed that free radical intermediates are not formed during the oxidation, which suggests two electron transfer mechanism during the oxidation of monohydric and polyhydric alcohols.

Fig. 8 Plot of ($10^4 k'$) versus $[ROH]$ in QDC reactions at 303 K. $[KHSO_4] = 0.167 \text{ mol/dm}^3$; $10^4 [QDC] = 1.33 \text{ mol/dm}^3$

Table 1 Concentration dependent rate constants of alcohol by [Quin-bound Cr(VI)] reagents in aqueous $KHSO_4$ media at 303 K

Cr(VI) reagent	[Alcohol] (mol/dm ³)	Ethylene glycol		Glycerol	
		($10^4 k'/\text{min}$)	(R^2)	($10^4 k'/\text{min}$)	(R^2)
QCC	0.083	2.00	0.997	4.00	0.992
	0.167	4.00	0.993	9.00	0.994
	0.333	7.00	0.998	20.0	0.991
	0.667	10.0	0.993	40.0	0.994
	1.00	20.0	0.991	60.0	0.993
QDC	0.083	4.00	0.986	6.00	0.978
	0.167	5.00	0.984	14.0	0.982
	0.333	10.0	0.987	30.0	0.980
	0.667	20.0	0.976	80.0	0.985
	1.00	30.0	0.985	100	0.986

Table 2 Concentration dependent rate constants of alcohol by [Quin-bound Cr(VI)] reagent in aqueous $KHSO_4$ media at 303 K

[Cr(VI)] reagent	[Alcohol] (mol/dm ³)	Erythritol		Xylitol		Sorbitol		Mannitol	
		$10^4 k' (\text{min})$	(R^2)	$10^4 k' (\text{min})$	(R^2)	$10^4 k' (\text{min})$	(R^2)	$10^4 k' (\text{min})$	(R^2)
QCC	0.042	6.00	0.998	12.0	0.987	14.0	0.997	14.0	0.997
	0.083	13.0	0.997	26.0	0.970	30.0	0.989	30.0	0.996
	0.167	30.0	0.988	60.0	0.998	70.0	0.998	60.0	0.997
	0.333	50.0	0.999	150.	0.997	160.0	0.991	140.0	0.989
	0.500	70.0	0.998	180.	0.988	200.0	0.996	190.0	0.987
QDC	0.042	6.0	0.998	20.0	0.999	20.0	0.998	42.0	0.998
	0.083	10.0	0.997	40.0	0.998	40.0	0.998	87.0	0.997
	0.167	30.0	0.999	90.0	0.998	100.0	0.999	120.0	0.998
	0.333	70.0	0.999	180.0	0.999	230.0	0.997	180.0	0.996
	0.500	90.0	0.997	260.0	0.998	300.0	0.996	300.0	0.996

3 Results and discussion

3.1 Order of the reactions

Plots of $\ln [A_0/A_t]$ versus time were found to be linear, passing through origin indicating first order dependence in $[QDC]$ or $[QCC]$, when $[Alcohol]$ is taken large excess over $[Quin-Cr(VI)]$ [Here, A_0 and A_t are the absorbance values (optical density) at zero time and at any instant of time (t) respectively (Figs. 1, 2, 3 and 4). Pseudo first order rate constant values (k') were obtained from the slopes of these plots at different concentrations of alcohols. Perusal of the obtained first order rate constant (k') values increased with an increase in the first power exponent raised to $[Alcohol]$, which reveal first order kinetics in $[Alcohol]$ (Figs. 5, 6, 7 and 8; Tables 1 and 2).

In order to gain an insight into the nature of reactive species, effect variation of ionic strength (μ) was studied using $NaClO_4$ in the concentration range of (0.01–0.10 mol/dm³) on the rate of QCC and QDC oxidation of polyols. But rate of oxidation was not affected to any considerable extent, which may indicate the participation of both primary salt arising from slow step, and secondary salt effect arising from involvement of acid–base equilibria prior to the rate limiting step, which may negate each other. A perusal of literature also depict that variation of ionic strength (μ) on reaction rate is either very small or negligible on ion–dipole, and dipole–dipole reactions [44, 45]. We have also studied the effect of variation of added $[KHSO_4]$ at constant $[Alcohol]$, and ionic strength (μ) of 0.200 (by

Fig. 9 Plot of ($10^4 k'$) versus $[KHSO_4]$ in QCC-Polyol reactions at 303 K. $[Polyol] = 0.167 \text{ mol/dm}^3$; $10^4 [QCC] = 1.33 \text{ mol/dm}^3$; $\mu = 0.200$

Fig. 10 Plot of ($10^4 k'$) versus $[KHSO_4]$ in QDC-Polyol reactions at 303 K. $[Polyol] = 0.083 \text{ mol/dm}^3$; $10^4 [QDC] = 1.33 \text{ mol/dm}^3$; $\mu = 0.200$

Fig. 11 Gibbs-Helmholtz plot for QDC oxidation of glycerol in $KHSO_4$ medium

maintaining with added $NaClO_4$. Under these conditions, variation of added $[KHSO_4]$ enhanced the observed rate constant (k') by ten fold, showing first order dependence on $[KHSO_4]$. Further, the plot of (k') versus $[KHSO_4]$ was linear with positive slope passing through origin confirmed that QDC-polyol, and QCC-polyol reactions occur only in presence of $KHSO_4$ (Figs. 9 and 10). When we have conducted kinetic experiments in the absence of $KHSO_4$, we

Fig. 12 Gibbs-Helmholtz plot for QCC oxidation of xylitol in $KHSO_4$ medium

have noticed that the reactions were too sluggish even at elevated temperatures. Therefore, all the kinetic experiments were taken up in aqueous bisulfate media at constant bisulfate concentration. Second order rate constants (k) were obtained from the slopes of (k') versus $[Alcohol]$ plots. An increase in temperature increased the rate constants (k) increased with temperature. Free energy of activation ($\Delta G^\#$) using the following equation, using Eyring's theory of reaction rates [44–46]:

$$(k) = (k_t)(R/Nh) \exp(-\Delta G^\# / RT) \quad (1)$$

In this equation (k_t) is known as the transmission coefficient, which is generally equal to unity. Further, by taking natural logarithms, Eq. (1) can be written as,

$$\Delta G^\# = RT \ln (RT/Nhk) \quad (2)$$

Substitution of gas constant (R), Avagadro Number (N), and Planck's constant (h) values (in SI units) into Eq. (2), $\Delta G^\#$ simplified could be further simplified to Eq. (3),

$$\Delta G^\# = 8.314 \times T [23.7641 + \ln (T/k)] \quad (3)$$

Free energy of activation ($\Delta G^\#$) can be obtained with proper substitution of rate constant (k) and temperature (T) values in Eq. (3). Enthalpy and entropies of activation ($\Delta H^\#$ and $\Delta S^\#$) values can then be obtained from the intercept and slope of the Gibbs-Helmholtz plot of ($\Delta G^\#$) versus temperature (T) according to Eq. (4).

$$\Delta G^\# = \Delta H^\# - T \Delta S^\# \Rightarrow \Delta G^\# = (-T \Delta S^\# + \Delta H^\#) \quad (4)$$

According to the above equation, plot of ($\Delta G^\#$) versus (T) should afford a straight line with a negative slope and intercept on ordinate, but in practice, either positive or negative slope may be obtained depending on the nature of the transition state (Figs. 11 and 12).

Scheme 1 Oxidation of alcohols by Quin-Cr(VI) reagents (QCC and QDC) **Fig. 13** Amis plot of (log k) versus (1/D) for QDC-Erythritol reaction. [Erythritol]=0.083 mol/dm³; 10⁴[QDC]=1.33 mol/dm³; Temp=305 K

3.2 Reactive species and mechanism of oxidation

Literature reports show that Cr(VI) exists in several reactive forms such as HCrO_4^- , H_2CrO_4 , $[\text{HCrO}_3]^+$ and CrO_3BH (where B = HSO_4^- , ClO_4^- , Cl^-) in aqueous acidic solutions [1, 2]. Basically QDC is known to exist as $[(\text{QH})_2\text{Cr}_2\text{O}_7]$ as it resembles $\text{K}_2\text{Cr}_2\text{O}_7$. In aqueous solutions it may hydrolyse in according to the following equilibrium:

Fig. 14 Kirkwood plot of $(\log k)$ versus $(D - 1/2D + 1)$ for QDC-Erythritol reaction. $[\text{Erythritol}] = 0.083 \text{ mol/dm}^3$; $10^4[\text{QCC}] = 1.33 \text{ mol/dm}^3$; $\text{Temp} = 305 \text{ K}$

In aqueous bisulfate solutions $[\text{H}(\text{QH})\text{CrO}_4]$ may form $[(\text{QH})\text{CrO}_3^+]$ (species (I)) due to protonation by abstracting proton released from the dissociation of bisulfate ion,

Species (I) further combines with polyol (ROH) in the slow step to give products as detailed in Scheme 1 (QDC path). Participation cationic and molecular $[(\text{QH})\text{CrO}_3^+]$ cation and R-OH in the rate-determining step, could be supported by the observed linearity of Amis plot of $(\log k)$ versus $(1/D)$, which gave a positive slope, as well as the linearity of Kirkwood plot of $(\log k)$ versus $(D - 1/2D + 1)$. These plots are shown in Figs. 13 and 14 respectively.

For the mechanism given in steps (6)–(8), rate law could be derived considering Eq. (8), as rate determining step. Accordingly, rate of the reaction could be written as,

$$\frac{-d[\text{QDC}]}{dt} = k[(\text{QH})\text{CrO}_3^+][\text{ROH}] \quad (9)$$

From Eq. (7) $[(\text{QH})\text{CrO}_3^+]$ could be written as,

$$[(\text{QH})\text{CrO}_3^+] = K_1 [\text{H}(\text{QH})\text{CrO}_4] [\text{H}^+] \quad (10)$$

Substituting for $[\text{H}^+]$ from Eq. (6),

$$[(\text{QH})\text{CrO}_3^+] = K_d K_1 [\text{H}(\text{QH})\text{CrO}_4] [\text{HSO}_4^-] / [\text{SO}_4^{2-}] \quad (11)$$

Now, substitution of $[(\text{QH})\text{CrO}_3^+]$ from Eq. (11) into Eq. (9) gives,

$$\frac{-d[\text{QDC}]}{dt} = k K_d K_1 [\text{H}(\text{QH})\text{CrO}_4] [\text{HSO}_4^-] [\text{ROH}] / [\text{SO}_4^{2-}] \quad (12)$$

Therefore, at constant $[\text{HSO}_4^-]$, rate Eq. (12) could be written as,

Fig. 15 Amis plot of $(\log k)$ versus $(1/D)$ for QCC-Erythritol reaction. $[\text{Erythritol}] = 0.167 \text{ mol/dm}^3$; $10^4[\text{QDC}] = 1.33 \text{ mol/dm}^3$; $\text{Temp} = 305 \text{ K}$

Fig. 16 Kirkwood plot of $(\log k)$ versus $(D - 1/2D + 1)$ for QCC-Erythritol reaction. $[\text{Erythritol}] = 0.167 \text{ mol/dm}^3$; $10^4[\text{QCC}] = 1.33 \text{ mol/dm}^3$; Temp = 305 K

$$\frac{-d[\text{QDC}]}{dt} = k'' [\text{QDC}][\text{ROH}] \quad (\text{Where } k'' = kK_dK_1[\text{HSO}_4^-] / [\text{SO}_4^{2-}]) \quad (13)$$

However, in the case of quinolinium chlorochromate (QCC) reactive species differ from QDC reactions. In aqueous acid medium, quinolinium chlorochromate (QCC) is known to exist as $[(\text{QH})\text{OCrO}_2\text{Cl}]$ and its protonated form $[(\text{QH})\text{OCrO}(\text{OH})\text{Cl}]^+$, by capturing proton (H^+) released from the dissociation of bisulfate ion according to the following equilibrium.

In this study protonated form of QCC $[(\text{QH})\text{OCrO}(\text{OH})\text{Cl}]^+$ appeared to be more active species than unprotonated form of QCC, since the reactions are accelerated by KHSO_4 .

Participation cationic $(\text{QH})\text{OCrO}(\text{OH})\text{Cl}^+$ cation and R-OH molecule in the rate-determining step, could be further supported by the observed linearity of Amis plot of $(\log k)$ versus $(1/D)$, which gave a positive slope,

as well as the linearity of Kirkwood plot of $(\log k)$ versus $(D - 1/2D + 1)$. These plots are shown in Figs. 15 and 16 respectively.

For the Eq. (15) rate law comes out as,

$$\frac{-d[\text{QCC}]}{dt} = k[(\text{QH})\text{OCrO}(\text{OH})\text{Cl}^+][\text{ROH}] \quad (16)$$

From Eq. (14) $[(\text{QH})\text{OCrO}(\text{OH})\text{Cl}^+]$ could be written as,

$$[(\text{QH})\text{OCrO}(\text{OH})\text{Cl}^+] = K_2[(\text{QH})\text{OCrO}_2\text{Cl}][\text{H}^+] \quad (17)$$

Here, Substituting for $[\text{H}^+]$ from Eq. (6),

$$[(\text{QH})\text{OCrO}(\text{OH})\text{Cl}^+] = K_dK_2[(\text{QH})\text{OCrO}_2\text{Cl}][\text{HSO}_4^-]/[\text{SO}_4^{2-}] \quad (18)$$

Now, substitution of $[(\text{QH})\text{OCrO}(\text{OH})\text{Cl}^+]$ from Eq. (18) into Eq. (9) gives,

$$\frac{-d[\text{QCC}]}{dt} = kK_dK_2[(\text{QH})\text{OCrO}_2\text{Cl}][\text{HSO}_4^-][\text{ROH}]/[\text{SO}_4^{2-}] \quad (19)$$

Therefore, at constant $[\text{HSO}_4^-]$, rate Eq. (19) could be simplified as,

$$\frac{-d[\text{QCC}]}{dt} = k'' [\text{QCC}][\text{ROH}] \quad (\text{Where } k'' = kK_dK_2[\text{HSO}_4^-] / [\text{SO}_4^{2-}]) \quad (20)$$

Table 3 Temperature dependant rate constants and activation parameters for the oxidation of polyhydroxy compounds by [Quin-bound Cr(VI)] reagent in aqueous KHSO₄ media

Quin-Cr(VI) reagent	Substrate	Temperature	10 ² k'' (dm ³ /mol/s)	ΔG [#] (kJ/mol)	ΔH [#] (kJ/mol)	– ΔS [#] (J/K/mol)
QCC	EG	293	0.150	87.6	30.2	196
		313	0.400	91.1		
		323	0.480	93.7		
	Glycerol	293	0.350	85.5	39.2	158
		313	1.20	88.3		
		323	1.59	90.4		
	Erythritol	293	1.10	82.7	33.2	169
		313	3.10	85.8		
		323	4.10	87.9		
	Xylitol	293	2.20	81.0	31.7	168
		313	6.50	83.9		
		323	7.90	86.2		
	Mannitol	293	2.10	81.2	41.3	136
		313	7.30	83.6		
		323	10.3	85.4		
	Sorbitol	293	2.70	80.5	32.4	164
		313	8.20	83.3		
		323	9.70	85.6		
QDC	Glycerol	293	1.35	82.2	55.7	91.0
		313	5.50	84.3		
		323	12.4	84.9		
	Erythritol	293	4.86	79.1	40.6	131
		313	17.8	81.3		
		323	24.2	83.1		
	Xylitol	293	8.80	77.7	43.9	115
		313	31.0	79.8		
		323	49.6	81.2		
	Mannitol	293	8.70	77.7	37.7	136
		313	28.0	80.1		
		323	40.0	81.8		
	Sorbitol	293	13.0	76.7	35.4	141
		313	31.0	79.8		
		323	57.0	80.8		

Thus, on the basis of the foregoing kinetic features and discussions, most plausible mechanistic steps for the oxidation of alcohols by QCC and QDC could be schematically represents as shown in Scheme 1.

In the above scheme QCC mechanistic route shows the participation of [(QH)OCrO(OH)Cl]⁺, while QDC route shows the participation of [(QH)Cr₃⁺] along with alcohol in the rate limiting step. The rate law for the mechanism given in Scheme 1, at constant bisulfate concentration, could be generally written as,

$$-\frac{d[\text{Quin} - \text{Cr(VI)}]}{dt} = k''[\text{Quin} - \text{Cr(VI)}][\text{ROH}]$$

The rate law is in consonance with the observed reaction kinetics, i.e., first order dependence on both the reactants [Alcohol] as well as [Quin-Cr(VI)] ([QDC] or [QCC]) at constant bisulfate concentration (Table 3).

The observed negative values of ΔS[#] probably suggest a systematic arrangement of atoms during the formation of activated complex, which may be polar than the reactants in terms of the transition state. The overall entropy change ΔS[#] accompanying the formation of the activated complex is generally negative because an activated complex is formed between two or more molecules, there is a loss in the transitional energy [36–38]. The ΔG[#] values for all the reactions are by and large appeared to be constant which

may probably indicate that a similar type of mechanism is operative in a reaction series.

4 Conclusions

Kinetics of KHSO_4 mediated oxidation of certain polyols by Quinolinium bound Cr(VI) reagents like quinolinium dichromate (QDC) and quinolinium chlorochromate (QCC) revealed second order kinetics with a first order dependence on [alcohol] and [Quin-Cr(VI) reagent] at constant bisulfate concentration.

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Compliance with ethical standards

Conflict of interest Authors declare that we don't have any conflict of interest related to this work.

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