Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2017, 6 (6): 1139-1148
(International Peer Reviewed Journal)

Oxidation of Some Vicinal and Non-Vicinal Diols by Imidazolium Dichromate: A Kinetic and Mechanistic Study

Shobha Puniya[1], Bhagyalaxmi[1], Rajesh Kumar[1], Gifty Sharma[1], PTSRK Prasadrao[2] and Vinita Sharma[1*]

1. Chemical kinetics laboratories, Department of Chemistry, J.N.V. University, Jodhpur, **INDIA**
2. Department of Chemistry, PB Siddharth College of Arts & Science, Vijayawada, A.P, **INDIA**

Email: drpkvs27@yahoo.com

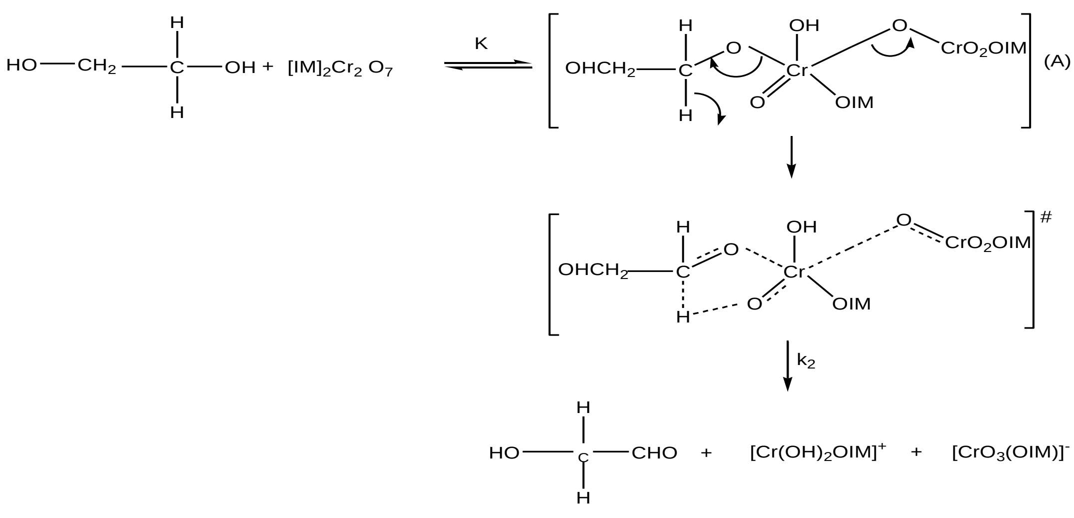
Accepted on 4th November 2017, Published online on 27th November 2017

ABSTRACT

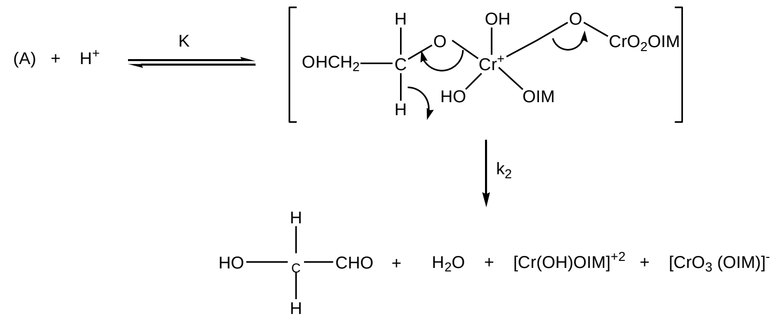
The kinetics of oxidation of four vicinal, four non-vicinal diols by imidazolium dichromate (IDC) have been studied in dimethylsulphoxide (DMSO). The main product of oxidation is the corresponding hydroxycarbonyl compound. The reaction is first order in IDC. Michaelis-Menten type of kinetics is observed with respect to the diols. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of $[1,1,2,2\text{-}^2H_4]$ ethanediol exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.75$ at 298 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical transition state in the rate-determining step. A suitable mechanism has been proposed.

Graphical Abstract

Acid-independent Path



Acid-dependent Path



Keywords: Correlation analysis, dichromate, diols, kinetics, mechanism, oxidation.

INTRODUCTION

Inorganic salts of Cr(VI) are well known oxidants for the organic compounds. However, these salts are rather drastic and non-selective oxidants. Further, they are insoluble in most organic solvents. Thus, miscibility is a problem. To overcome these limitations, a large number of derivatives of Cr(VI) have been prepared and used in organic synthesis as mild and selective oxidants in non-aqueous solvents [1-4]. Imidazolium dichromate (IDC) is one such compound used for the oxidation of aliphatic primary and secondary alcohols [5]. We have been interested in the kinetic and mechanistic aspects of the oxidation by complex salts of Cr(VI) and several reports on halochromates and dichromates have already reported from our laboratory [6-10]. There seems to be no report on the oxidation aspects of diols using imidazolium dichromate (IDC). Therefore, it was of interest to investigate the kinetics of the oxidation of some vicinal and non-vicinal diols by IDC in DMSO. A suitable mechanism has also been postulated.

MATERIALS AND METHODS

Materials: The diols and the monoethers (BDH or Fluka) were distilled under reduced pressure before use. IDC was prepared by the reported method [5]. [1,1,2,2-$^2H_4$] Ethanediol (DED) was prepared by reducing diethyl oxalate with lithium aluminium deuteride [11]. Its isotopic purity, determined by its NMR spectrum, was 96±3%. Due to the non-aqueous nature of the medium, toluene-p-sulphonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar solvent like DMSO, it is likely to be completely ionized.

Product analysis: Product analysis was carried out under kinetic conditions. In a typical experiment, ethanediol (0.1 mol) and IDC (0.01 mol) were taken in DMSO (100 mL) and the mixture was allowed to stand in the dark for ca. 10 h to ensure completion of the reaction. Most of the solvent was removed under reduced pressure and residue treated overnight with an excess (250 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl. The precipitated 2,4-dinitrophenylhydrazone(DNP) was filtered off, dried, recrystallized from ethanol and weighed. The product was found identical (m.p. and mixed m.p.) with an authentic sample of DNP of hydroxyethanol.

Kinetic measurements: The reactions were followed under pseudo-first order conditions keeping a large excess (x 15 or greater) of the diols over IDC. The temperature was kept constant to ±0.1K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of IDC spectrophotometrically at 354 nm for up to 80% of the reaction. No other reactant or product has any significant absorption at this wave-length. The pseudo-first order rate constants, k_{obs}, were evaluated from the linear (r = 0.995 - 0.999) plots of log [IDC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ±3%. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

RESULTS AND DISCUSSION

Stoichiometry: The homogeneity of the DNP derivatives indicated the formation of only one product in each case. Under our reaction conditions, therefore, there is no observable oxidation of the second hydroxy group. This may be due to the presence of a large excess of the diol over IDC. The overall reaction may, therefore, be written as equation (1).

$$3HOCH_2{-}CH_2OH + Cr_2O_7^{-2} + 8H^+ \longrightarrow 3HOCH_2{-}CHO + 7H_2O + 2Cr^{+3} \quad (1)$$

Kinetic Dependence: The reactions are of first order with respect to IDC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of IDC. Figure 1 depict a typical kinetic run. The reaction rate increases with increase in the concentration of the diols but not linearly (Table 1). A plot of $1/k_{obs}$ against 1/[Diol] is linear (r > 0.995) with an intercept on the rate-ordinate (Figure 2). Thus, Michaelis-Menten type kinetics are observed with respect to the diol. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

$$\text{Diol} + \text{IDC} \overset{\mathbf{K}}{\leftrightarrows} [\text{complex}] \quad (2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \quad (3)$$

$$\text{Rate} = k_2 K [\text{Diol}] [\text{IDC}] / (1 + K [\text{Diol}]) \quad (4)$$

Table 1. Rate constants for the oxidation of propan-1,2-diol by IDC at 298 K

10^3 [IDC] mol dm^{-3}	[Diol] mol dm^{-3}	10^4 k_{obs} s^{-1}
1.00	0.10	3.92
1.00	0.20	5.98
1.00	0.40	8.11
1.00	0.60	9.21
1.00	0.80	9.87
1.00	1.00	10.3
1.00	1.50	11.0
1.00	3.00	11.7
2.00	0.20	6.03
4.00	0.20	5.76
6.00	0.20	5.94
8.00	0.20	5.85
1.00	0.40	8.46*

[a] contained 0.001 M acrylonitrile

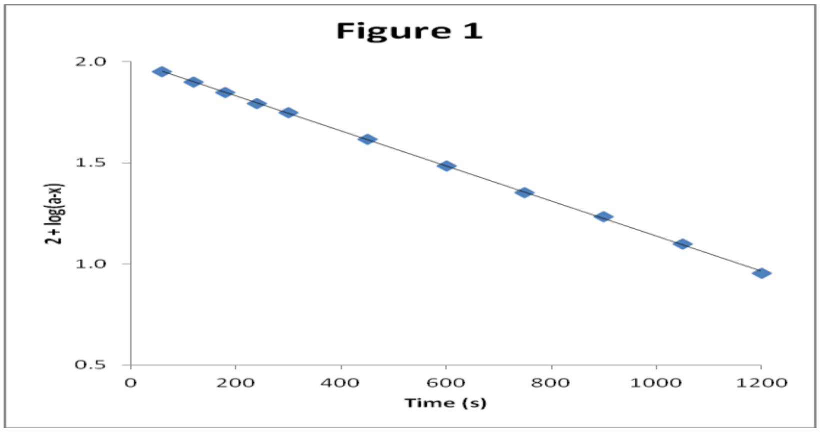


Figure 1. Oxidation of Ethane-diol by IDC at 308 K: A typical Kinetic Run

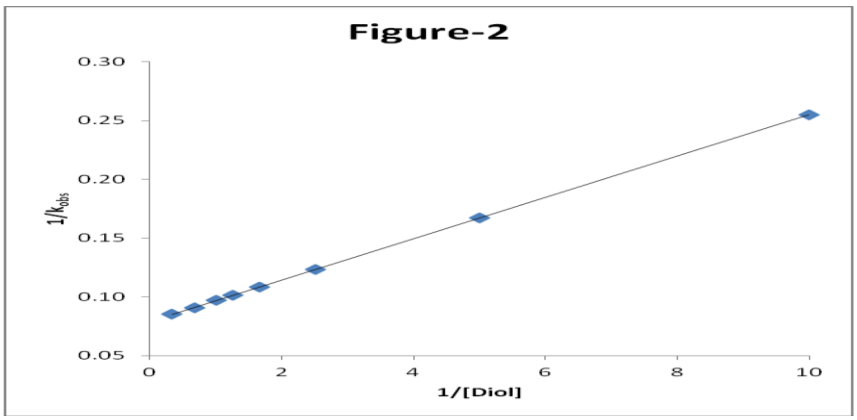


Figure 2. $1/k_{obs}$ vs 1/[Diol]: A double reciprocal plot

The dependence of reaction rate on the reductant concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2 respectively at different temperatures (Tables 3 and 4).

Test for free radicals: The oxidation of diols, by IDC, in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate (Table 1). To further confirm the absence of free radicals in the reaction pathway, the reaction was carried out in the presence of 0.05 mol dm^{-3} of 2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

Effect of hydrogen ions: The reaction is catalyzed by hydrogen ions (Table 2). The hydrogen-ion dependence has the form: $k_{obs} = a + b\,[H^+]$. The values of a and b for ethane diol are $3.98 \pm 0.19 \times 10^{-4}$ s^{-1} and $7.27 \pm 0.32 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9961$).

Table 2. Dependence of the reaction rate on hydrogen–ion concentration

[IDC] = 0.001 mol dm^{-3};		[Ethane Diol] = 1.0 mol dm^{-3};		Temp. = 318 K	
$[H^+]$/mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
10^4 k_{obs}/s^{-1}	4.68	5.49	6.75	8.28	10.2	11.0

Kinetic isotope effect: To ascertain the importance of the cleavage of the α-C-H bond in the rate-determining step, the oxidation of DED was studied. Results (Tables 2 and 3) showed the formation constants, K, of the intermediate complex of the deuteriated and protiated diols do not differ much, however, the rate of disproportionation of the intermediate exhibited the presence of a substantial primary kinetic isotope (k_H/k_D = 5.75 at 298 K).

Table 3. Rate constants for the decomposition of IDC−Diol complexes and activation parameters

$10^4\ k_2$ / ($dm^3\ mol^{-1}\ s^{-1}$)					ΔH^*	$-\Delta S^*$	ΔG^*
Diols	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
Ethane-1,2	0.72	2.07	5.31	12.6	70.1±0.5	81±2	94.1±0.4
Propan-1,2	3.51	8.46	19.8	42.3	60.8±0.2	100±1	90.5±0.2
Butane-2,3	16.2	35.1	74.7	144	53.1±0.3	114±1	87.0±0.3
Butane-1,2	4.77	11.7	26.1	54.0	59.1±0.5	104±2	89.8±0.4
Propan-1,3	7.47	17.1	37.8	79.2	57.4±0.1	106±1	88.8±0.1
Butane-1,3	9.36	18.9	40.5	82.8	53.0±0.9	119±3	88.4±0.7
Butane-1,4	10.8	23.4	51.3	108	56.0±0.6	108±2	88.0±0.5
Pentane-1,5	15.3	31.5	66.6	135	52.9±0.7	116±2	87.2±0.5
DED	0.12	0.36	0.95	2.37	73.0±0.5	86±2	98.4±0.4
k_H/k_D	6.00	5.75	5.59	5.32			

Table 4. Formation constants for the decomposition of IDC−Diols complexes and thermodynamic parameters

K ($dm^3\ mol^{-1}$)					$-\Delta H^*$	$-\Delta S^*$	$-\Delta G^*$
Diols	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J $mol^{-1}K^{-1}$)	(kJ mol^{-1})
Ethane-1,2	6.71	5.94	5.27	4.52	70.1±0.5	81±2	94.1±0.4
Propan-1,2	6.54	5.80	5.13	4.39	60.8±0.2	100±1	90.5±0.2
Butane-2,3	5.95	5.22	4.50	3.78	53.1±0.3	114±1	87.0±0.3
Butane-1,2	5.84	5.14	4.41	3.70	59.1±0.5	104±2	89.8±0.4
Propan-1,3	6.14	5.40	4.72	3.96	57.4±0.1	106±1	88.8±0.1
Butane-1,3	6.85	6.12	5.44	4.68	53.0±0.9	119±3	88.4±0.7
Butane-1,4	5.76	5.06	4.30	3.61	56.0±0.6	108±2	88.0±0.5
Pentane-1,5	6.03	5.35	4.59	3.86	52.9±0.7	116±2	87.2±0.5
DED	5.81	5.10	4.39	3.67	73.0±0.5	86±2	98.4±0.4

Effect of organic solvents: The oxidation of ethanediol was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of IDC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The values of formation constants K and decomposition constants of the complex, k_2 are recorded in Table 5.

Table 5. Effect of solvents on the oxidation of Propan-1,2-diol by IDC at 298 K

Solvents	K (dm^{-3} mol^{-1})	10^4 k_{obs} (s^{-1})	Solvents	K (dm^{-3} mol^{-1})	10^4 k_{obs} (s^{-1})
Chloroform	5.76	38.9	Toluene	4.98	12.0
1,2-Dichloroethane	5.85	47.9	Acetophenone	5.48	56.2
Dichloromethane	6.03	35.5	THF	4.99	22.4
DMSO	5.14	117	t-Butylalcohol	5.06	13.5
Acetone	6.11	43.7	1,4-Dioxane	5.80	24.5
DMF	5.04	58.9	1,2-Dimethoxyethane	5.44	10.5
Butanone	5.69	32.4	CS_2	6.00	6.46
Nitrobenzene	5.55	55.0	Acetic Acid	5.57	7.08
Benzene	5.60	14.8	Ethyl Acetate	5.88	17.8
Cyclohexane	6.13	1.86			

The correlation between activation enthalpies and entropies of the oxidation of diols is linear (r = 0.9718), indicating the operation of a compensation effect [12]. The value of the isokinetic temperature is 533±51 K. However, according to Exner [13], an isokinetic relationship between the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between log k_2 at 288 K and at 318 K was linear (r = 0.9987; Figure 3). The value of isokinetic temperature evaluated from the Exner's plot is 622±64 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in the rate are governed by changes in both the enthalpy and entropy of activation.

Solvent effect: The rate constants, k_2, for the oxidation of ethanediol in 18 organic solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) did not exhibit any significant correlation in terms of the linear solvation energy relationship (5) of Kamlet et al., [14].

$$\log k_2 = A_0 + p c^* + b\beta + a\alpha \qquad (5)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 13 have a value of zero for α. The results of correlation analyses in terms of equation (5), a biparametric equation involving π^* and β, and separately with π^* and β are given below equations (6) - (9).

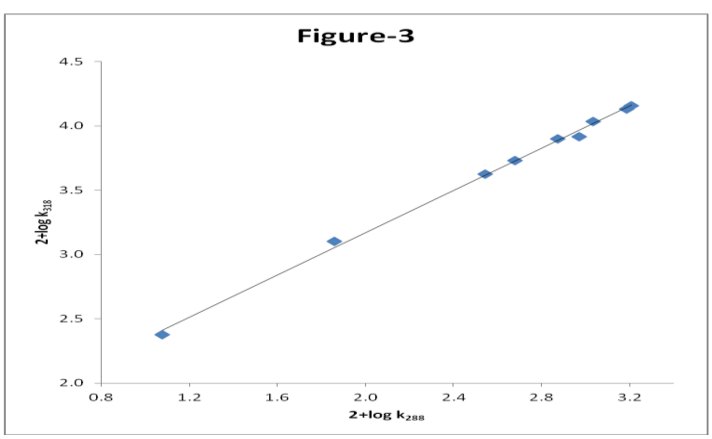


Figure 3. Exner's Isokinetic Relationship in the oxidation of Diols by IDC

$\log k_2 = -4.36 + 1.51 (\pm 0.20)\, \pi^* + 0.15 (\pm 0.16)\, \beta - 0.18 (\pm 0.15)\, \alpha$ (6)
$R^2 = 0.8495$; sd = 0.18; $n = 18$; $\Psi = 0.42$
$\log k_2 = -4.32 + 1.58 (\pm 0.19)\, \pi^* + 0.09 (\pm 0.15)\, \beta$ (7)
$R^2 = 0.0659$; sd = 0.42; $n = 18$; $\Psi = 0.99$
$\log k_2 = -4.34 + 1.60 (\pm 0.18)\, \pi^*$ (8)
$r^2 = 0.8308$; sd = 0.18; $n = 18$; $\Psi = 0.42$
$\log k_2 = -3.71 + 0.38 (\pm 0.34)\, \beta$ (9)
$r^2 = 0.0715$; sd = 0.41; $n = 18$; $\Psi = 0.99$

Here n is the number of data points and ψ is the Exner's statistical parameter [15].

Kamlet's [14] triparametric equation explains *ca.* 85% of the effect of solvent on the oxidation. However, by Exner's criterion [10] the correlation is not even satisfactory (*cf.* equation 6). The major contribution is of solvent polarity. It alone accounted for *ca.* 83% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's[16] equation (10) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \quad (10)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. (A + B) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of equation (11), separately with A and B and with (A + B).

$\log k_2 = 0.50 (\pm 0.05)\, A + 1.64 (\pm 0.04)\, B - 3.85$ (11)
$R^2 = 0.9917$; sd = 0.04; $n = 19$; $\Psi = 0.10$
$\log k_2 = 0.27 (\pm 0.54)\, A - 2.73$ (12)
$r^2 = 0.0142$; sd = 0.44; $n = 19$; $\Psi = 1.02$
$\log k_2 = 1.60 (\pm 0.10)\, B - 3.69$ (13)
$r^2 = 0.9427$; sd = 0.11; $n = 19$; $\Psi = 0.24$
$\log k_2 = 1.26 \pm 0.15\, (A + B) - 3.82$ (14)
$r^2 = 0.8092$; sd = 0.19; $n = 19$; $\Psi = 0.45$

The rates of oxidation of ethanediol in different solvents showed an excellent correlation in Swain's equation (cf. equation 11) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 99% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 81% of the data. In view of the fact that solvent polarity is able to account for *ca.* 81% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not linear ($r^2 = 0.5091$; sd = 0.31; $\psi = 0.72$).

Correlation analysis of reactivity: The rates of oxidation of the four vicinal diols in DMSO showed the excellent correlation with Taft's σ^* values [17] with negative reaction constants (Table 6), this indicates the presence of an electron-deficient rate-determining step. Here $\Sigma \sigma^*$ represents the sum of the substituent constants for the substituents present on the two alcoholic carbons of the vicinal diols. The fact that σ^* values alone able to account for 99% of the data showed that steric factors do not play any significant role in the reaction. The magnitude of the reaction constants decreases with an increase in the temperature, indicating that selectivity decreases with an increase in the reactivity.

Table 6. Reaction constants of the oxidation of vicinal diols by IDC

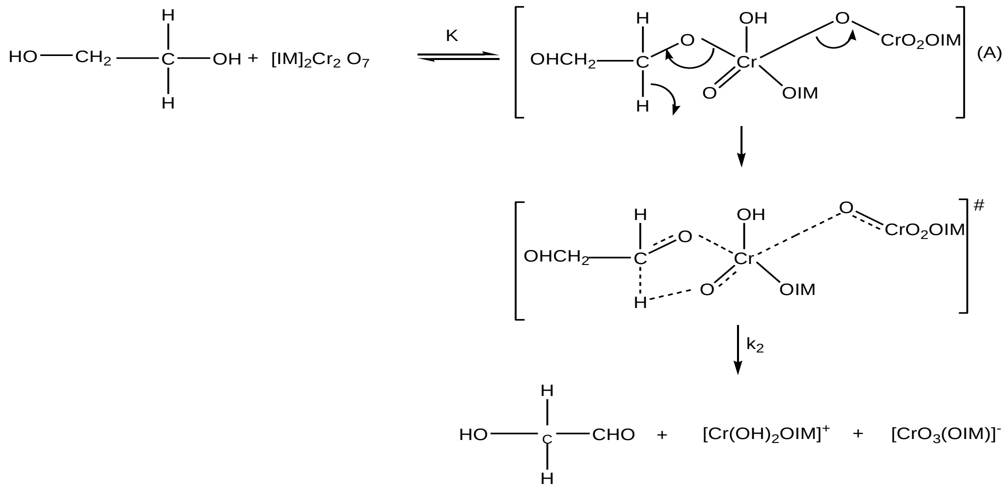
Temp./ K	$-\rho^*$	r^2	Sd	ψ
288	1.38±0.11	0.9868	0.08	0.13
298	1.26±0.11	0.9845	0.08	0.14
308	1.17±0.09	0.9873	0.06	0.13
318	1.08±0.08	0.9885	0.06	0.12

Mechanism: The presence of a substantial primary kinetic isotope effect confirms the cleavage of an α-C-H bond in the rate-determining step. The negative values of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state has an electron-deficient carbon centre. Hence the transfer of a hydride-ion from diol to the oxidant is suggested. The hydride-transfer mechanism is also supported by the major role of cation-solvating power of solvents.

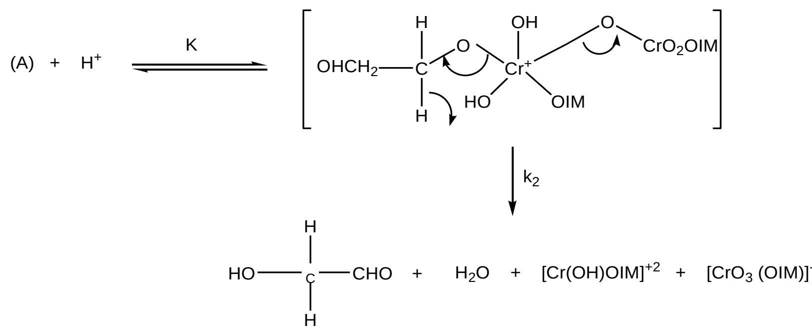
The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. Kwart and Nickle [18] have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem. The data for protio- and deuterio-ethandiols, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp (E_a /RT)$ [19,20] show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference (ΔE_a) for k_H/k_D is equal to the zero-point energy difference for the respective C-H and C-D bonds ($\approx$ 4.5 kJ mol^{-1}) and the frequency factors and the entropies of activation of the respective reactions are nearly equal. Bordwell [21] has documented a very cogent evidence against the occurrence of concerted one-step bimolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic bimolecular process. It is well established that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer [22].

Littler [23] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and, being a Huckel-type system, is an allowed process. Thus, the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Scheme 1). The observed hydrogen-ion dependence can be explained by assuming a rapid reversible protonation of the chromate ester (A) with the protonated ester decomposing at a rate faster than (A) (Scheme 2).

It is of interest to recall that pinacol is oxidized by chromic acid but not by IDC. Chatterjee and Mukherji [24] reported an abrupt change from butane-2,3-diol to pinacol, the latter reacting very fast. As pointed out by Littler [23], a cyclic ester mechanism is forbidden in the diol-Cr(VI) reaction. Chromic acid oxidation of pinacol may therefore involve two one- electron steps. Chromic acid oxidations are known to induce polymerization of acrylamide under certain conditions [25]. No such observation has yet been recorded with IDC. Thus, the capability of chromic acid and the inability of IDC to act as a one-electron oxidant may explain the different behaviour of pinacol towards these two oxidants.



Scheme-1 Acid-independent Path



Scheme-2 Acid-dependent Path

ACKNOWLEDGEMENTS

Thanks are due to the UGC & DST New Delhi, for financial support as in the form of scholarship to (Rajesh) Inspire Fellowship to GS respectively.

REFERENCES

[1] G. Cainelli and G. Cardillo, *Chromium oxidations in organic chemistry*, (Springer-Verlag, Berlin) **1984**, Vol. 19.
[2] H. Firouzabadi and A. Sharifi, *Synthesis*, **1992**, 999.
[3] M. Li and M.E. Johnson, *Synth. Communn.*, **1995**, 25, 533.
[4] M.K. Mahanti and K.K. Banerji, *J. Indian Chem. Soc.*, **2002**, 79, 31.
[5] S. Kim and DC Lhim, *Bull. Chem. Soc. Jpn.*, **1986**, 59, 3297.
[6] A. Sharma, A. Meena J. Khatri, P. Swami and Vinita Sharma, *J. Applicable Chem.*, **2012**, 1(1)**,** 70.
[7] N. Vyas, A. Daiya, A. Choudhary, M. Sharma and Vinita Sharma, *Eur. Chem. Bull.*, **2013**, 2(11), 859.
[8] N. Vyas, G. Goswami, A. Choudhary, PTSRK Prasadrao and Vinita Sharma, *Int. J. Chem.*, **2015**, 4(3) 215.
[9] Anamika Choudahry, Sonali Saraf, Shobha Poonia, and Vinita Sharma, *J. Applicable Chem.*, **2016**, 5(4) 861.
[10] I. Hedau, J. Solanki, R. Sharma, U. Songara and Vinita Sharma, *J. Applicable Chem.*, **2017**, 6(5), 846.

[11] T.J. Kemp and W.A. Waters, *Proc Roy Soc Ser A*, **1963**, 274, 480.
[12] L. Liu and W.E. Guo, *Chem. Review*, **2001**, 101, 673.
[13] O. Exner, *Collect. Chem. Czech. Commun.*, **1977**, 38, 411.
[14] M.J. Kamlet, J L M Abboud, M H Abraham, R W Taft, *J. Org. Chem.*, **1983**, 48, 2877.
[15] O. Exner, *Collect. Chem. Czech. Commun.*, **1966**, 31, 3222.
[16] C.G. Swain, M.S. Swain, A.L. Powel and S. Alunni, *J. Am. Chem. Soc.*, **1983**, 105, 502.
[17] K. B. Wiberg, *Physical Organic Chemistry*, Wiley, New York, **1963**, p. 416.
[18] H. Kwart and J.H. Nickel, *J. Am. Chem. Soc*., **1953**, 95, 3394.
[19] H. Kwart and M.C. Latimer, *J. Am. Chem. Soc.*, **1971**, 93, 3770.
[20] H. Kwart and J. Slutsky, *J. Chem. Soc. Chem. Commun*, **1972**, 1182.
[21] F.G. Bordwell, *Acc. Chem. Res.*, **1974**, 5, 374.
[22] R.W. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Eng.*, **1969**, 8, 781.
[23] J.S. Littler, *Tetrahedron*, **1971**, 27, 81.
[24] A.C. Chatterjee and S.K. Mukherji, **1957**, **1958**, **1960**, *Z Phys Chem*, 207, 372, 208, 281; 210, 166.
[25] M. Rahman and J. Rocek, **1971**; **1972**, *J Am Chem Soc*, 93, 5462; 94, 3181.

AUTHORS' ADDRESSES

1. **Shobha Puniya**
Research Scholar, Department of Chemistry,
J.N.V. University, Jodhpur
E-mail: shobhapuniya@gmail.com
2. **Bhagyalaxmi**
Research Scholar, Department of Chemistry,
J.N.V. University, Jodhpur
E-mail: laxmigehlot90@gmail.com
3. **Rajesh Kumar**
Research Scholar, Department of Chemistry,
J.N.V. University, Jodhpur
E-mail: rajeshkchoudhary89@gmail.com
4. **Gifty Sharma**
DST,Inspire Fellow,
Department of Chemistry,
J.N.V. University, Jodhpur,
E-mail: gifty.shrm@gmail.com
5. **PTSRK Prasadrao**
Assistant Professor, Department of Chemistry,
PB Siddharth College, Vijaywada, A.P.
E-mail: posaniprasadrao@yahoo.co.in
6. **Vinita Sharma**
Professor, Department of Chemistry,
J.N.V. University, Jodhpur
E-mail: drvsharma29@gmail.com