



# OXIDATION OF ALIPHATIC PRIMARY ALCOHOLS BY TETRAKIS (PYRIDINE) SILVER DICHROMATE – A KINETIC AND MECHANISTIC APPROACH

Amit Daiya<sup>[a]</sup>, Deepika Sharma<sup>[a]</sup>, Manju Baghmar<sup>[b]</sup>, Pallvi Mishra<sup>[a]</sup>,  
Shobha Sharma<sup>[a]</sup> and Vinita Sharma<sup>[a]\*</sup>

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The oxidation of nine aliphatic primary alcohols by tetrakis(pyridine) silver dichromate (TPSD) in dimethylsulfoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to TPSD. A Michaelis-Menten type kinetics is observed with respect to alcohols. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form  $k_{obs} = a + b [H^+]$ . The oxidation of  $[1,1-^2H_2]$ ethanol ( $MeCD_2OH$ ) exhibits a substantial primary kinetic isotope effect ( $k_H/k_D = 5.85$  at 298 K). The reaction has been studied in nineteen different organic solvents. The solvent effect was analysed using Taft's and Swain's multiparametric equations. The rate of oxidation is susceptible to both polar and steric effects of the substituents. A suitable mechanism has been proposed.

\* Corresponding Authors

Fax: +91 291 2721880

E-Mail: [drvsharma29@gmail.com](mailto:drvsharma29@gmail.com)

[a] Department of Chemistry, J.N.V. University, Jodhpur, India

[b] Department of Chemistry, University of Rajasthan, Jaipur, India

## Introduction

Inorganic chromate and dichromate salts have been used as oxidizing reagents in synthetic organic chemistry for long time. However, these salts are drastic and non-selective oxidants in nature and as ionic compounds generally insoluble in most of the organic solvents. In order to overcome these limitations, a large number of organic derivatives of Cr(VI) have been prepared and used in synthetic organic syntheses as mild and selective oxidants in non-aqueous solvents.<sup>1</sup>

One such compound is tetrakis(pyridine)silver dichromate (TPSD) reported by Firouzabadi and co-workers.<sup>2</sup> Only a few reports are available in literature regarding oxidation aspects of TPSD.<sup>3</sup> It is known that the mode of oxidation depends on the nature of the counter-ion attached to the chromium anion. Therefore, in continuation of our earlier work, we report here the kinetics and mechanism of oxidation of nine aliphatic primary alcohols by TPSD in dimethylsulphoxide (DMSO) as solvent. The mechanistic aspects are discussed.

The main aims of the present investigation are to (i) determine kinetic parameters and to evaluate the rate laws, (ii) to study the correlation analysis of effect of structure on (iii) and to postulate a suitable mechanism for the oxidation process.

## Experimental Section

### Materials

TPSD was prepared by the reported method<sup>2</sup> and its purity was checked by an iodometric method. The procedures used for the purification of alcohols have been described earlier.<sup>4</sup>  $[1,1-^2H_2]$ Ethanol ( $MeCD_2OH$ ) was prepared by Kalpan's method.<sup>5</sup> Its isotopic purity, as ascertained by its NMR spectra, was  $96 \pm 3\%$ . Due to the non-aqueous nature of the medium, p-toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. TsOH is a strong acid and in a polar medium like DMSO it is likely to be completely ionised. Solvents were purified by the usual method.<sup>6</sup>

### Product analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (2.30 g, 0.05 mol) and TPSD (7.48 g, 0.01 mol) were made up to 50  $cm^3$  in DMSO and kept in dark for *ca.* 15 hr to ensure the completion of the reaction. The solution was then treated with an excess (200  $cm^3$ ) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol  $dm^{-3}$  HCl 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 before and after recrystallization was 1.98 g (91%) and 1.84 g (81%), respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. Similar experiments with other alcohols led to the formation of DNP of the corresponding carbonyl compounds in yields ranging from 72 to 87%, after recrystallization. Iodometric determinations of the oxidation state of chromium in completely reduced reaction mixtures indicated that the oxidation state of the reduced chromium species was  $3.90 \pm 0.10$ .

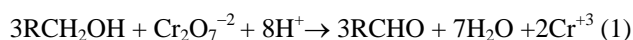
### Kinetic Measurements

The reactions were followed under pseudo-first-order conditions by keeping a large excess ( $\times 15$  or greater) of the alcohol over TPSD. The temperature was kept constant to  $\pm 0.1$  K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of TPSD spectrophotometrically at 365 nm for 80% of the reaction. The pseudo-first-order rate constants,  $k_{obs}$ , were evaluated from the linear ( $r = 0.990 - 0.999$ ) plots of  $\log [TPSD]$  against time. Duplicate kinetic runs showed that the rate constants were reproducible to within  $\pm 3\%$ . The second order rate constant,  $k_2$ , was evaluated from the relation  $k_2 = k_{obs}/[\text{alcohol}]$ . Simple and multivariate linear regression analyses were carried out by the least-squares method on a personal computer.

## Results and Discussion

### Stoichiometry

The oxidation of alcohols results in the formation of corresponding aldehydes. The overall reaction may be represented as equation (1).



### Rate-laws

The reactions are of first order with respect to TPSD. Further, the pseudo-first order rate constant,  $k_{obs}$  is independent of the initial concentration of TPSD. The reaction rate increases with increase in the concentration of the alcohols but not linearly (Table 1).

**Table 1.** Rate constants for the oxidation of ethanol by TPSD at 288 K

$10^3 [TPSD]$ mol dm <sup>-3</sup>	[Alcohol] mol dm <sup>-3</sup>	[TsOH] mol dm <sup>-3</sup>	$10^4 k_{obs}$ s <sup>-1</sup>
1.00	0.10	0.00	18.9
1.00	0.20	0.00	27.6
1.00	0.40	0.00	35.9
1.00	0.60	0.00	39.9
1.00	0.80	0.00	42.3
1.00	1.00	0.00	43.8
1.00	1.50	0.00	46.0
1.00	3.00	0.00	48.5
2.00	0.20	0.00	29.7
4.00	0.20	0.00	26.1
6.00	0.20	0.00	30.6
8.00	0.20	0.00	27.0
1.00	0.40	0.00	37.8*

\* contained 0.001 mol dm<sup>-3</sup> acrylonitrile

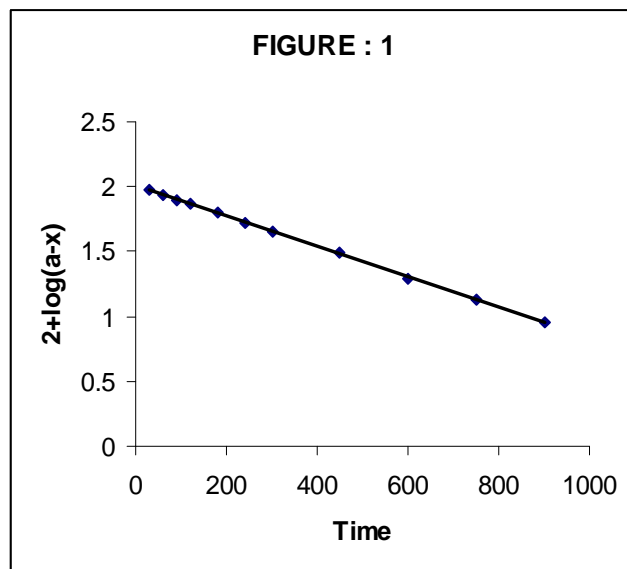
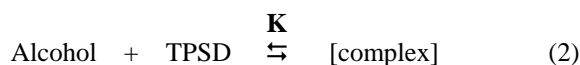


Figure 1. Oxidation of Ethyl alcohol by TPSD: A typical Kinetic Run

The Figure 1 depicts a typical kinetic run. A plot of  $1/k_{obs}$  against  $1/[\text{Alcohol}]$  is linear ( $r > 0.995$ ) with an intercept on the rate-ordinate. Thus, Michaelis-Menten type kinetics is observed with respect to alcohols. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).



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

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 (Figure 2). 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 2 and 3).

### Induced Polymerization of Acrylonitrile

The oxidation of alcohols, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile did not affect the rate. This indicates that a one-electron oxidation, giving rise to free radicals, is unlikely in the present reaction (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<sup>-3</sup> of 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxytoluene or BHT). It was observed that BHT was recovered unchanged, almost quantitatively.

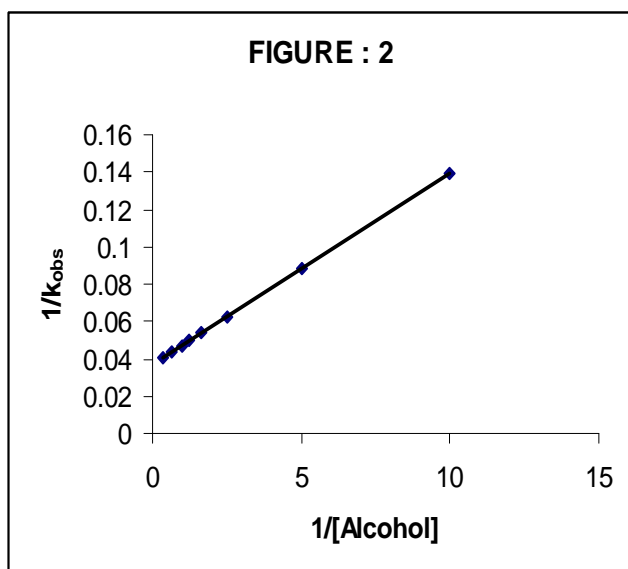


Figure 2. Oxidation of Alcohols by TPSD: A double reciprocal plot

### Effect of Hydrogen Ions

The reaction is catalyzed by hydrogen ions (Table 4). The hydrogen-ion dependence has the following form equation (5). The values of  $a$  and  $b$ , for ethanol, are  $18.6 \pm 0.07 \times 10^{-4} \text{ s}^{-1}$  and  $31.8 \pm 0.12 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  respectively ( $r^2 = 0.9999$ ).

$$k_{\text{obs}} = a + b [\text{H}^+] \quad (5)$$

### Kinetic Isotope Effect

To ascertain the importance of cleavage of the  $\alpha$ -C-H bond in the rate-determining step, oxidation of  $[1,1\text{-}^2\text{H}_2]$ ethanol was studied. The results showed the presence of a substantial primary kinetic isotope effect (Table 3).

### Effect of Solvents

The oxidation of ethanol was studied in 19 different organic solvents. The choice of solvent was limited due to the solubility of TPSD and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of  $k_2$  are recorded in Table 5.

A satisfactory linear correlation ( $r = 0.9824$ ; temp.  $449 \pm 32$ ) between the values the activation enthalpies and entropies of the oxidation of the nine aliphatic alcohols indicated the operation of compensation effect in this reaction.<sup>7</sup> The reaction also exhibited an excellent isokinetic effect, as determined by Exner's criterion.<sup>8</sup> An Exner's plot between  $\log k_2$  at 288K and at 318 K was linear ( $r = 0.9961$ ;  $\psi = 0.07$ ; slope =  $0.7744 \pm 0.0261$ ) (Figure 3). The value of isokinetic temperature is  $500 \pm 43$  K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and the changes in rate are governed by the changes in both the enthalpy and entropy of the activation.

### Solvent Effect

The rate constants of the oxidation,  $k_2$ , in eighteen solvents ( $\text{CS}_2$  was not considered, as the complete range of solvent parameters was not available) did not yield any significant correlation in terms of the linear solvation energy relationship (LESR) of Kamlet and Taft<sup>9</sup> (6).

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (6)$$

$$\log k_2 = -4.24 + 1.59 (\pm 0.20)\pi^* + 0.19 (\pm 0.16)\beta + 0.14 (\pm 0.16)\alpha \quad (7)$$

$$R^2 = 0.8586; \text{ sd} = 0.18; n = 18; \psi = 0.41$$

$$\log k_2 = -4.21 + 1.64 (\pm 0.19)\pi^* + 0.15 (\pm 0.15)\beta \quad (8)$$

$$R^2 = 0.8508; \text{ sd} = 0.18; n = 18; \psi = 0.40$$

$$\log k_2 = -4.24 + 1.68 (\pm 0.18)\pi^* \quad (9)$$

$$r^2 = 0.8415; \text{ sd} = 0.18; n = 18; \psi = 0.41$$

$$\log k_2 = -2.83 + 0.44 (\pm 0.36)\beta \quad (10)$$

$$r^2 = 0.0865; \text{ sd} = 0.43; n = 18; \psi = 0.98$$

Here  $n$  is the number of data points and  $\psi$  is the Exner's statistical parameter.<sup>10</sup> Kamlet's<sup>9</sup> triparametric equation explains *ca.* 86% of the effect of solvent on the oxidation. However, by Exner's criterion<sup>10</sup> the correlation is not even satisfactory (cf. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 86% of the data. Both  $\beta$  and  $\alpha$  play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's<sup>11</sup> equation (11) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \quad (11)$$

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 eq. (12), separately with  $A$  and  $B$  and with  $(A+B)$ .

$$\log k_2 = 0.63 (\pm 0.04)A + 1.71 (\pm 0.03)B - 3.98 \quad (12)$$

$$R^2 = 0.9957; \text{ sd} = 0.03; n = 19; \psi = 0.07$$

$$\log k_2 = 0.39 (\pm 0.56)A - 2.81 \quad (13)$$

$$r^2 = 0.0271; \text{ sd} = 0.46; n = 19; \psi = 1.01$$

$$\log k_2 = 1.66 (\pm 0.11)B - 3.77 \quad (14)$$

$$r^2 = 0.9248; \text{ sd} = 0.13; n = 19; \psi = 0.27$$

$$\log k_2 = 1.35 \pm 0.14 (A+B) - 3.95 \quad (15)$$

$$r^2 = 0.8463; \text{ sd} = 0.18; n = 19; \psi = 0.40$$

Here  $n$  is the number of data points and  $\psi$  is the Exner's statistical parameter.<sup>10</sup>

**Table 2.** Formation constants and thermodynamic parameters for the Alcohol – TPSD complexes

Subst.	$K$ (dm <sup>3</sup> mol <sup>-1</sup> )				$-\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$-\Delta S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>	$-\Delta G^\ddagger$ kJ mol <sup>-1</sup>
	288 K	298 K	308 K	318 K			
H	6.03	5.25	4.40	3.62	15.5±0.6	30±2	6.55±0.5
Me	5.85	5.02	4.25	3.45	15.8±0.6	32±2	6.46±0.5
Et	5.40	4.61	3.75	3.00	17.4±0.7	38±2	6.22±0.6
n-Pr	5.76	4.92	4.12	3.35	16.2±0.6	33±1	6.40±0.5
n-Bu	6.12	5.30	4.52	3.67	15.3±0.7	30±2	6.59±0.6
i-Pr	5.33	4.55	3.70	2.95	17.5±0.8	39±3	6.18±0.6
ClCH <sub>2</sub>	5.62	4.80	4.02	3.20	16.7±0.8	35±3	6.34±0.6
MeOCH <sub>2</sub>	6.15	5.35	4.50	3.72	15.3±0.6	30±1	6.60±0.5
t-Bu	5.90	5.10	4.26	3.45	16.1±0.7	33±2	6.48±0.6
MeCD <sub>2</sub> OH	5.98	4.18	4.35	3.56	15.6±0.6	31±2	6.52±0.5

**Table 3.** Rate constants and activation parameters for the Alcohols – TPSD complexes

Alcohol (R)	$10^4 k_2 / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ at}$				$\Delta H$ kJ mol <sup>-1</sup>	$-\Delta S$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G$ kJ mol <sup>-1</sup>
	288 K	298 K	308 K	318 K			
H	0.81	2.81	9.00	27.0	86.4±0.1	23±1	95.0±0.6
Me	51.3	117	261	558	58.1±0.3	87±1	84.9±0.4
Et	87.3	189	414	846	55.3±0.5	93±2	83.6±0.7
n-Pr	153	315	621	1260	50.8±0.7	104±2	82.2±0.2
n-Bu	162	342	693	1350	51.3±0.1	101±1	81.9±0.3
i-Pr	243	477	954	1800	48.5±0.5	108±2	81.0±0.3
ClCH <sub>2</sub>	0.98	2.61	7.02	17.1	70.3±0.5	78±2	94.7±0.5
MeOCH <sub>2</sub>	8.10	19.8	47.7	108	63.3±0.3	85±1	89.4±0.3
t-Bu	2250	3510	5400	7920	29.5±0.1	155±1	75.5±0.1
MeCD <sub>2</sub> OH	8.29	20.0	46.6	105	61.9±0.3	89±1	89.2±0.4
k <sub>H</sub> /k <sub>D</sub>	6.19	5.85	5.60	5.31			

The rates of oxidation of ethanol in different solvents showed an excellent correlation in Swain's equation (cf. equation 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 92% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 86% of the data. In view of the fact that solvent polarity is able to account for *ca.* 86% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of log k<sub>2</sub> against the inverse of the relative permittivity is not linear ( $r^2 = 0.5313$ ;  $sd = 0.32$ ;  $\psi = 0.70$ ).

### Correlation Analysis of Reactivity

The rates of oxidation of the alcohols failed to yield any significant correlation separately with Taft's<sup>12</sup>  $\sigma^*$  and E<sub>s</sub> values eqs. (16) and (17).

$$\log k_2 = -2.17(\pm 0.33) \Sigma \sigma^* - 1.73 \quad (16)$$

$$r^2 = 0.8584; \quad sd = 0.42; \quad \psi = 0.40; \quad n = 9$$

$$\log k_2 = -1.13(\pm 0.36) \Sigma E_s - 2.28 \quad (17)$$

$$r^2 = 0.5804; \quad sd = 0.73; \quad \psi = 0.69; \quad n = 9$$

The rates were, therefore, correlated in terms of Pavelich-Taft's<sup>13</sup> dual substituent-parameter (DSP) equation (19).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \quad (19)$$

The values of substituent constants were obtained from the compilation by Wiberg<sup>12</sup>. The correlations are excellent; the reaction constants being negative (Table 6). There is no significant collinearity ( $r^2 = 0.2322$ ) between  $\sigma^*$  and E<sub>s</sub> values of the nine substituents.

The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The negative steric reaction constant shows a steric acceleration of the reaction. This may be explained on the basis of high ground state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde as well as in the transition state leading to it, the transition state energies of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore, results.

### Mechanism

The presence of a substantial primary kinetic isotope effect confirms the cleavage of an  $\alpha$ -C-H bond in the rate-determining step. The large negative value of the polar reaction constant together with substantial deuterium isotope effect indicate that the transition state approaches a carbocation in character. Hence the transfer of hydride-ion from alcohol to the oxidant is suggested. The hydride-transfer mechanism is also supported by the major role of cation-solvating power of the solvents (Scheme 1).

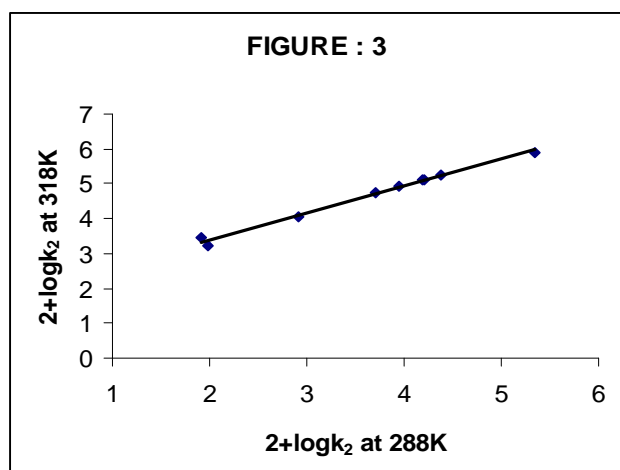


Figure 3. Exner's Isokinetic Relationship in the oxidation of Alcohols by TPSD

The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. This postulation is supported by an analysis of the temperature dependence of kinetic isotope effect. Kwart and Nickle<sup>14</sup> have shown that a study of the dependence of the kinetic isotope effect on temperature can be gainfully employed to resolve this problem.

**Table 4.** Dependence of the reaction rate on hydrogen-ion concentration, [Alcohol]=0.10 mol dm<sup>-3</sup>; [TPSD]=0.001 mol dm<sup>-3</sup>; Temp. 298 K

[TsOH]/ mol dm <sup>-3</sup>	0.10	0.20	0.40	0.60	0.80	1.00
$10^4 k_{obs}/s^{-1}$	21.8	24.9	31.5	37.8	44.1	50.4

**Table 5.** Effect of solvents on the oxidation of alcohols by TPSD at 308 K

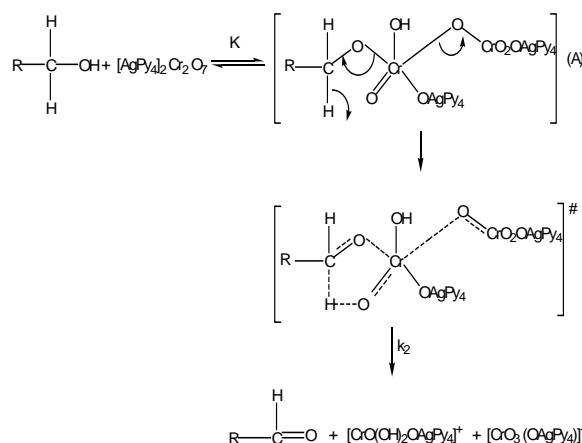
Solvents	K (dm <sup>-3</sup> mol <sup>-1</sup> )	$10^5 k_2$ (s <sup>-1</sup> )
Chloroform	6.11	36.3
Toluene	5.27	9.77
1,2-Dichloroethane	5.48	41.7
Acetophenone	4.48	56.2
Dichloromethane	4.63	38.9
THF	4.29	18.2
DMSO	5.02	117
t-butylalcohol	5.22	15.1
Acetone	4.81	32.4
1,4-Dioxane	4.36	17.4
DMF	5.58	63.1
1,2-Dimethoxyethane	5.55	11.0
Butanone	4.79	27.5
CS <sub>2</sub>	4.78	5.25
Nitrobenzene	4.95	49.0
Acetic acid	5.43	6.46
Benzene	5.36	12.0
Ethyl acetate	4.76	15.8
Cyclohexane	5.18	1.45

**Table 6.** Temperature dependence of the reaction constant

T, K	$-\rho^*$	$-\delta$	$r^2$	sd	$\psi$
288	1.80±0.01	0.73±0.01	0.9999	0.010	0.01
298	1.71±0.02	0.63±0.01	0.9998	0.005	0.02
308	1.62±0.01	0.54±0.02	0.9989	0.002	0.04
318	1.55±0.02	0.45±0.02	0.9999	0.007	0.01

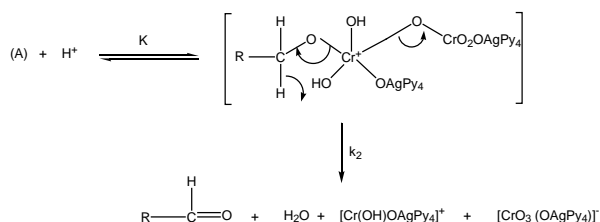
The data for protio- and deuterio-ethanols, fitted to the familiar expression  $k_H/k_D = A_H/A_D \exp(E_a/RT)$ <sup>15</sup> show a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference ( $\Delta E_a$ ) for  $k_H/k_D$  is equal to the zero-point energy difference for the respective C-H and C-D bonds ( $\approx 4.5$  kJ/mol) and the frequency factors and the entropies of activation of the respective reactions are nearly equal.

Acid-independent Path (Scheme -1)



The similar phenomena have also been observed earlier in the reactions of halochromates. Bordwell<sup>16</sup> 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<sup>17</sup>. Littler<sup>18</sup> 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).

Acid-dependent Path (Scheme - 2)



## Conclusion

The reaction is proposed to proceed through a hydride-ion transfer from alcohol to the oxidant in the rate-determining step. It has also been observed that an  $\alpha$ -C-H bond is cleaved in the rate-determining step. Both deprotonated and protonated forms of TPSD are the reactive oxidising species.

## Acknowledgements

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