KINETICS AND MECHANISM OF THE OXIDATION OF ALIPHATIC ALCOHOLS BY BUTYLTRIPHENYLPHOSPHONIUMDICHROMATE

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1. INTRODUCTION

Selective oxidation of organic compounds under non-aqueous conditions is an important transformation in synthetic organic chemistry. For this, a number of different chromium (VI) derivatives have been reported.[1,2] In 1997, Baltork *et al*[3] reported a new Cr(VI) derivative - butyltriphenylphosphonium dichromate (BTPPD). BTPPD is reported to convert alcohols to corresponding carbonyl compounds in yields ranging from 80 to 100%. It oxidises amines to azo-compounds, thiols to disulphides and regenerate carbonyl compounds from their oximes. We have been interested in the kinetics and mechanisms of the oxidations by BTPPD and some reports on the oxidation by BTPPD have emanated from our labpratory.[4-6] In this paper, we report the kinetics of the oxidation of some aliphatic primary and secondary alcohols by BTPPD in dimethylsulphoxide (DMSO) as the solvent. Mechanistic aspects are discussed.

2. EXPERIMENTAL

Materials.- BTPPD was prepared by the reported method and its purity was checked iodometrically. The alcohols were commercial products and were purified by the usual methods. The solvents were purified by the usual methods.[7] [l,l-^{2}H2]Ethanol and

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[2-^{2}H]propan-2-ol were prepared by the reported methods.[8*9] Their isotopic purity, as ascertained by their H NMR spectra, was 92±4% and 90±5% respectively. As the solvent was non-aqueous, toluene p-sulphonic acid (TsOH) was used as a source of hydrogen ions.

Product Analysis.- The product analyses were performed under kinetic conditions i.e., with an excess of alcohol over the oxidant. In a typical experiment, 2-propanol (0.3 mol), TsOH (0.05 mol), and BTPPD (0.02 mol) were made up to 100 ml in QMSO and was allowed to stand in the dark for *ca.* 10 h to ensure completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm"^{3} HC1 and was. kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yield of DNP, before and after recrystallization was 1.41 g (91%) and 1.32 g (85%) respectively. The DNP was found identical (mp and mixed mp) with the DNP of acetone. In similar experiments, with other alcohols, the yield of the corresponding carbonyl compounds was in the range of 80-92%, after recrystallization.

Kinetic Measurements.- The reactions were studied under pseudo-first-order conditions by keeping an excess (x 10 or greater) of the alcohol over BTPPD. The solvent was DMSO, unless otherwise specified. The reactions were studied at constant temperature (±0.1 K) and were followed by monitoring the decrease in the [BTPPD] spectrophotometrically at 364 nm for up to 80% reaction. The Beer's law is valid for BTPPD within the concentration range used in our experiments. The pseudo-first-order rate constants, kobs, were evaluated from linear plots ($r > 0.9990$) of log [BTPPD] against time. Duplicate kinetic runs showed that the rates were reproducible to within ±3%. The specific rate constant, k, was evaluated from the relation: $k = kobs / [alcohol]^2 [H^+]^2$

3. RESULTS

The oxidation of alcohols by BTPPD yielded the corresponding carbonyl compounds as the main product. The overall reaction can be represented as equation (1).

$$3\ R_2CHOH + Cr_20_7^{"2} + 8\ H^+ \text{-►}\ 3\ R_2C{=}0 + 7\ H_20 + 2\ Cr^{+3} \quad (l)$$

Induced Polymerisation of Acrylonitrile. The oxidation of the alcohols, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. Further, the rate of oxidation is nol affected by the addition of acrylonitrile (Table 1).

The reaction is first order with respect to BTPPD. Further, th(pseudo-first-order rate constant, kobs, does not depend on the initia concentration of BTPPD. The reaction showed a second orde: dependence on the concentration of alcohol (Table 1).

Table 1. Rate constants for the oxidation of alcohols by BTPPD

10^3[BTPPD]	[Alcohol]	10^4kobs(s-')	
(mol $dm^{'3}$)	(mol $dm^{"3}$)	Ethanol"	2-Propanol[b]
1.0	0.1	1.80	1.60
1.0	0.2	7.00	6.52
1.0	0.3	15.5	14.4
1.0	0.5	44.7	41.0
1.0	0.7	85.7	80.1
1.0	1.0	176	164
0.5	0.5	45.3	40.5
2.0	0.5	45.0	42.0
3.0	0.5	43.9	41.6
5.0	0.5	44.2	40.9
1.0	0.5[C]	45.0	40.7

[a] [FT"] = 1.00 mol dm^{-3}; Temperature = 318 K;[b] [H+] = 0.20 mol $dm^{"3}$; Temperature = 288 K
[c] contained 0.001 mol $dm^{"3}$ acrylonitrile

Effect of Acidity.- The rate of oxidation of of the alcohols increases with an increase in the concentration of hydrogen ions. The reaction is second order with respect to the acid (Table 2).

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

$[H^+]$	lO'kobsCs"^{1})	
(mol dm"^{3})	Ethanol"	2-Propnaol^D
0.05	0.433	0.410
0.10	1.73	1.65
0.20	6.87	6.64
0.30	15.8	14.6
0.50	42.9	41.3
0.75	97.0	93.2
1.00		176
164		

* [alcohol] = 1.00 mol dm"^{3}; Temperature = 318 K

^{b} [alcohol] = 0.20 mol dm"^{3}; Temperature = 288 K

Effect of substituents.- The rates of oxidation of fifteen primary and secondary aliphatic alcohols were determined at different temperatures and the activation parameters were calculated (Tables 3 and 4).

Table 3. Rate constants for the oxidation of alcohols by BTPPD

Alcohol	10^4k(mol $l^4 dm^{12} s^{-1}$)			
	288K	298K	308K	318K
Methanol	0.011	0.039	0.146	0.570
2-Chloro-ethanol	0.041	0.140	0.455	1.74
2-ethanol	0.660	1.98	6.23	22.1
Ethanol	6.72	19.9	59.3	176
1-Chloro-propanol-2	23.6	58.7	160	451
1-Propanol	15.5	41.0	111	336
1 -Butanol	37.3	93.1	267	802
1-Pentanol	43.8	115	305	802
2-Methyl-propanol-1	77.2	194	485	1390
1-Methoxy-propanol-2	380	853	2210	6130
2-Propanol	4050	9300	21400	50000
2-Butanol	5740	11200	25300	61800-
2-Pentanol	21700	40500	92000	202000
3-Methyl-butanol-2	45700	86000	176000	385000
2-Hexanol	26600	51000	106000	235000

Table 4. Activation parameters of the oxidation of alcohols by BTPPD.

Alcohol	AH* kJ mol^{-1}	AS* J mol^{-1} K^{-1}	AG* kJ mol
Methanol	97.6±2.1	-2213	10412.0
2-Chloroethanol	91.9±2.4	-3014	10112.1
2-Methoxy-ethanol	86.2±2.0	-2614	94.012.0
Ethanol	79.9±3.0	-2914	88.512.1
1-Chloro-propanol-2	72.1±1.6	-46+4	85.511.6
1 -Propanol	75.0±2.0	-3913	86.511.7
1-Butanol	75.4+2.0	-3112	84.411.7
1-Pentanol	71.311.0	-4312	84.010.8
2-Methylpropanol-1	70.5±2.1	-4213	82.711.4
1-Methoxy-propanol-2	68.1±1.7	-3712	78.911.4
2-Propanol	61.211.0	-4112	73.110.9
2-Butanol	57.811.2	- 5013	72.511.2
2-Pentanol	54.611.7	-5013	69.311.8
3-Methylbutanol-2	51.512.0	-5413	67.511.6
2-Hexanol	52.711.9	-5514	68.811.5

Kinetic Isotope Effect- To ascertain the importance of the cleavage of the a-C-H bond in the rate-determining step, the oxidation of deuteriated ethanol and 2-propanol was studied. The oxidation exhibited a substantial primary kinetic isotope effect (Table 5).

Table 5. Kinetic isotope effect in the oxidation of ethanol and 2-propanol by BTPPD

Alcohol	lO^Cmol^dm'V)			
	288K	298K	308K	318K
Ethanol	6.72	19.9	59.3	176
[U-$^2H_2$]-ethanol	1.07	3.34	10.4	32.7
k_H/k_D	6.28	5.96	5.69	5.38
2-Propanol	4050	9300	21400	50000
[2-^{2}H]-2-propanol	774	1870	4510	11200
k_H/k_D	5.23	4.97	4.75	4.48

Solvent Effect.- The oxidation of 2-propanol by BTPPD was studied in nineteen organic solvents. The solubility of the reactants and the reaction of BTPPD with primary and secondary alcohols limited the choice of solvents. There was no reaction with the chosen solvents. The kinetics were similar in all the solvents. The values of the rate constant, k, are recorded in Table 6.

Table 6. Effect of solvent on the oxidation of 2-propanol by BTPPD at 298 K

Solvent	10^3k	Solvent	10^3 k
	(mol^{-4} dm'V)		(mor^{4}dm^{12} s^{-1})
Chloroform	242	Toluene	82.7
1.2-Dichloroethane	275	Acetophenone	371
Dichloromethane	282	Tetrahydronfuran	133
DMSO	930	t-BuOH	105
Acetone	263	Dioxane	138
Dimethylformamide	440	Butanone	204
Acetic acid	43.2	Cyclohexane	12.0
Nitrobenzene	318	Ethyl acetate	118
Benzene	110	Carbon disulfide	44.6
1,2-Dimethoxy-ethane	78.2		

4. DISCUSSION

The values of log k at 288 K, for the fifteen alcohols, are linearly related to log k at 318 K (slope = 0.8821±0.0032; r^2 = 0.9995). The value of isokinetic temperature is 1458+162 K. Current views do **not** attach much significance to value of isokinetic temperature.[10] A linear isokinetic relationship is, however, a necessary condition **for** the validity of linear free energy relationships.[10] It also implies **that** all the reactions, so correlated, follow a similar mechanism.

Solvent Effect.- The values of the rate constant, k, in eighteen solvents (CS2 was not considered as the complete range of the solvent parameters are not available), was correlated in terms of linear solvation energy relationship (LSER) of Kamlet *et al.*"

logk = A + pir +aoc + bp (

Here *n** represents the solvent polarity for solvent-sol interaction of non-specific type, p is a scale of solvent hydrogi bond acceptor basicity, while a represents the solvent hydrogi bond donor acidity; A is the intercept term. It may be mentior here that out of the 18 solvents, for 13 solvents a has a value zero. The analyses in terms of equation (2), a two-parame

equation involving *n** and p, and separately with *n** and p gave i following results [equations (3) - (6)].

logk= -1.83+ 1.5010.19 it*-0.20±0.15 a+ 0.20±0.16p (3) R^2 = 0.8534, sd = 0.18, n = 18,y = 0.30

logk= -1.87+1.58±0.19TC* +0.13±0.16p (4)
R^2 = 0.8347, sd = 0.18, n = 18,i|/ = 0.31

logk= -1.85 +1.61±0.18TI* (5)
r^2 = 0.8271, sd = 0.18, n = 18, y = 0.31

logk= -0.95 + 0.41+0.35 p (6)
r^2 = 0.0806, sd = 0.42, n= 18,vj/ = 0.87

Here n is the number of data points, sd is the standard deviati and *i* is the Exner's statistical parameter. The results show that *ca.* 85% of the data on the solvent effect explained by equation (2). According to Exner's criterion however, the correlation is poor. The major contribution is frc the solvent polarity term, *n**, *[cf.* eqn. (5)], both a and p playi relatively insignificant roles. The data on solvent effect were analysed in terms of Swaii equation (7) also, where A represents the anion-solvating power the solvent and B the cation-solvating power; C is the interce term, and (A + B) is postulated to represent the solvent polarity.[1,1]
log k = aA + bB + C (7)

The results of the correlation analyses in terms of equation (' individually with A and B, and with (A + B) are given below.

log k = 0.49±0.03 A + 1.65±0.02 B - 2.03 (8)
R^2 = 0.9977, sd = 0.02, ft = 19,\|/ = 0.03

log k = 0.26±0.55 A - 0.90 (9)
j ^ = 0.0129, sd = 0.44, n=19,vj/ = 0.97

log k=1.62±0.09B- 1.87 (10)
r = 0.9508, sd = 0.10, n = 19,i)/= 0.16

logk= 1.27±0.15(A + B)-2.00 (11)
i **r** = 0.8095, sd = 0.19, n=19,\|/ = 0.33

The data on solvent effect showed an excellent correlation in terms of Swain's equation[13] with both anion- and cation-solvating powers contributing to the observed solvent effect. However, the **role** of cation-solvation is major, it alone accounts for *ca.* 95% of **die** data. The solvent polarity, represented by (A + B) accounted **for** *ca.* 81% of the data. In view of the fact *ca.* 81% of the data is accounted for by (A+B), attempt was made to correlate the data **with** the relative permittivity of the solvents. A plot of log k against the inverse of the relative permittivity, however, is not Snear (r^2 = 0.4988, sd = 0.31, y = 0.55).

The solvent polarity term of Kamlet's equation[11] explained *ca.* 83% of the data. Thus it seems that the solvent polarity terms of the two equations represent nearly the same solvent property. This is borne out by the fact that there is a significant collinearity between *x'* and (A + B) for the eighteen solvents (r^2 = 0.7811). *Correlation Analysis of Reactivity.*- Preliminary computation
: showed that the rate constants, k, of oxidation of the alcohols do **act** exhibit satisfactory correlation with either the polar or steric substituent parameters separately. Therefore, the rates were analysed in terms of dual substituent-parameter (DSP) equation
; leqn.(12)]ofPavelichandTaft.[14]

$$\log k = p^*\sigma^* + 5\ 2E_S + \log k_0 \quad (12)$$

Excellent correlations were obtained with the reaction constants being negative (Table 7). The negative steric reaction constant indicates a steric acceleration. 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/ketone as well as in the transition state leading to it, the transition state energies of the crowded and non-crowded alcohols do not differ much and a steric acceleration, therefore, results.

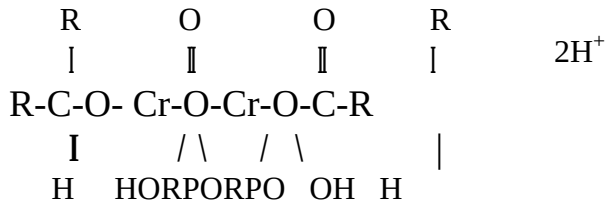
Table 7. Temperature dependence of the reaction constants

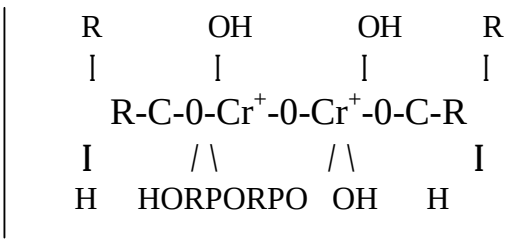
T/K	p*	5	R^2	sd	|/
288	-2.41±0.01	-1.2910.01	0.9999	0.01	0.008
298	-2.31±0.02	-1.23+0.02	0.9998	0.01	0.011
308	-2.23±0.02	-1.18±0.02	0.9996	0.02	0.015
318	-2.1510.03	-1.1210.02	0.9994	0.03	0.019

Mechanism.- The presence of a substantial primary kinetic isotope effect confirms the cleavage of the oc-C - H bond in the rate-determining step. A one-electron oxidation, giving rise to free, radicals, is unlikely in view of the failure to induce polymerisation of acrylonitrile. The analysis of the solvent effect indicated the importance of the cation-solvating power of the solvent. The negative polar reaction constants indicate the presence of an electron-deficient reaction centre in the transition state of the rate-determining step. Therefore, the transfer of a hydride ion from the alcohol to the oxidant is indicated. A hydride-ion transfer may take place either by- an acyclic process or *via* a chromate ester. Kwart and Nickle[15] have shown that a dependence of kinetic isotope effect on temperature can be gainfully employed to

determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic process. The data for protio- and deuterio-ethanols and 2-propanols fitted to the familiar expression: $k_H/k_D = A\backslash\backslash IA_D \exp(-AE_a / RT)$[16,17] showed a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference for ICH/ICD is equal to the zero-point energy difference for the respective C-H and C-D bonds *(ca.4.5* kJ mol"[1]) and the entropy of activation of the respective reactions are nearly equal. Bordwell[18] has given cogent evidence against the occurrence of concerted one-step bimolecular processes of hydrogen transfer and it is clear that in the present reaction also, the hydrogen transfer does not occur by an acyclic bimolecular process. The only truly symmetrical processes involving linear transfer of hydrogen are intrinsically concerted sigmatropic reactions characterized by transfer with a cyclic transition state.[19] Littler[20] has also shown that a cyclic hydride-ion transfer, in the oxidation of alcohols by Cr(VI), involves six electrons and being a Huckel type system, is an allowed process. Therefore, one can safely conclude that in the oxidation of alcohols by BTPPD, the hydride-ion transfer occurs *via* a chromate ester. Formation of ester intermediates in the oxidation of alcohols by Cr(VI) compounds is well documented.[21] The observed acid-dependence of the reaction points to a rapid reversible protonation of the ester intermediate prior to its disproportionation. A mechanism depicted in Scheme 1 accounts for the experimental results. It may be mentioned that though the formation of the diester and its diprotonation is shown as single steps, these must be taking place in two steps each.

$(R'P)2Cr_207 + 2R_2CHOH$ t;





-» 2 R_2 C = O + 2 H_20 + (R'P)2Cr_205 + 2 H^+
Cr(IV)

fast Cr(VI) -
> 2 Cr (V)

fast Cr(V) + Reductant -
> Product + Cr (III)

R P = butyltriphenyl

Scheme 1

Initially Cr(VI) is reduced to Cr(IV). It is likely to react with another Cr(VI) to generate Cr(V) which is then reduced in a fast step to the ultimate product Cr(III). Such a sequence of reactions in Cr(VI) oxidations is well known.[21]

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