KINETICS AND MECHANISM OF THE QUINOLINIUM FLUOROCHROMATE OXIDATION OF SOME PRIMARY, SECONDARY AND UNSATURATED ALCOHOLS IN ACETONITRILE

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Quinolinium fluorochromate (QFC) in MeCN readily oxidises primary and secondary alcohols to the corresponding carbonyl compounds. Solvent effect on reactivity is quite significant. The reaction can be characterized by the rate equation $v = k_3K_1K_2[\text{Alc}][\text{TsOH}][\text{QFC}]_t/ \{1 + [\text{TsOH}](K_1 + K_1K_2[\text{Alc}])\}$. The ρ^* value *ca* –1.6 is indicative of a partial bonding in the linear transition state envisaged. Large primary kinetic isotope effect ($k^H/k^D > 10$) in this study suggests a concerted, two-electron hydride transfer mechanism. Mechanistic studies on the oxidation of unsaturated alcohols with QFC in acetonitrile medium described by the rate equation $k_0 = k_2K_1[\text{TsOH}]^2 + k_4K_3K_1[\text{Alc}][\text{TsOH}]$ is verified. Product analysis studies rule out the possibility of attack on the double bond. Linear relation in the Exner plots implies the operation of a common mechanism in all the alcohols studied. The high reactivity observed in the cinnamyl alcohol oxidation can be ascribed to resonance interaction through conjugated double bonds.

Keywords: Alcohols; Quinolinium fluorochromate; Chromates; Oxidations; Aldehydes; Reaction kinetics; Reaction mechanisms; Solvent effects.

Among the selectively acting oxo derivatives of variable valence metals, chromium compounds play the most important role, because the oxidative reactions based on them can be readily carried out. The major use of Cr(VI) reagents in synthetic chemistry is in the oxidation of alcohols to carbonyl compounds. As a result, alcohol oxidation with these was extensively investigated. The number of new Cr(VI) reagents together with special reaction conditions have been developed. Anhydrous conditions are more conducive to complexation of substrates with Cr(VI) species and therefore to mild oxidation. The most significant recent Cr(VI) oxidants are quinolinium fluorochromate[1,2] (QFC), pyridinium chlorochromate[3,4] (PCC), pyridinium dichromate[5] (PDC), pyridinium fluorochromate[6–13] (PFC) and quinolinium chlorochromate[14] (QCC). QFC in dichloromethane readily oxidises primary, secondary and allylic alcohols to the corresponding carbonyl com-

pounds. Pandurangan *et al.*[15] reported the kinetics and mechanism of substituted benzyl alcohols with QFC in AcOH–H_2O medium. No kinetic and mechanistic study of the QFC oxidation of alcohols in anhydrous conditions have appeared. Here, we examine the kinetics and mechanism of oxidation of twelve primary and secondary alcohols and three unsaturated alcohols with QFC in acetonitrile medium. A comparison is also made with the corresponding reactions of structurally similar oxidants.

Coordination complexes of chromium can be used successfully for the conversion of hydroxy into carbonyl groups in unsaturated alcohols. The oxidation of unsaturated systems having functional groups as substituents finds applications in the synthesis of hormones, pheromones, prostaglandins and their synthones. The present study describes the kinetics of oxidation of three unsaturated alcohols, *viz.* allyl alcohol, but-2-en-1-ol and cinnamyl alcohol in acetonitrile medium.

EXPERIMENTAL

All the chemicals used were reagent grade products. The alcohols were dried over anhydrous magnesium sulfate and fractionally distilled before use. The reactions were performed under pseudo-first-order conditions by maintaining large excess (1 : 100 or higher) of alcohols over QFC. The reaction mixture was homogeneous throughout the course of the reaction. The reactions were followed by monitoring the decrease in absorption of QFC at 360 nm employing a JASCO 7200 UV-VIS spectrophotometer with a variable-temperature accessory. Duplicate kinetic runs showed that the rate constants obtained by titrimetric procedure agreed within ±3%. All the rate constants are average of two or more determinations.

The stoichiometry of the reaction was determined for a number of reaction mixtures containing at least a threefold excess of oxidant over the substrate. The estimation indicated that two moles of the oxidant reacted with three moles of the substrate.

$$3 \ RCH_2OH + 2 \ Cr(VI) \rightarrow 3 \ RCHO + 6 \ H^+ + 2 \ Cr(III)$$
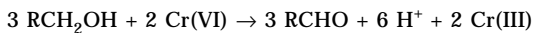
Oxidant (0.010 mol), methanol (0.015 mol) and 4-methylbenzene-1-sulfonic acid (TsOH; 0.015 mol) were mixed. After 24 h, the solvent was evaporated. The residue was extracted with ether and the product obtained was identified by the formation of 2,4-dinitrophenylhydrazones. The ketones were also detected by characteristic spot tests[16].

RESULTS AND DISCUSSION

Oxidation of Primary and Secondary Alcohols

Under pseudo-first-order conditions, it was observed that first-order plots showed curvature after 25–30% conversion of QFC, *i.e.*, the reaction in-

volves two distinct pathways – an initial rapid step followed by a slow one due to depletion of QFC (Fig. 1). The depressed reactivity observed after some time may probably be due to the influence of the products on the reaction. This is reminiscent of the effect noted by Ramachandran *et al.* in the study of HSO_5^- oxidation of amino acids[17]. In Br(V) oxidation of cinnamic acids[18] slow and subsequent fast reactions are attributed to two reactive species, Br(V) and molecular bromine. Initial-rate method was used to determine the order with respect to reactants in the oxidation of alcohols. A plot of k_0^{-1} *versus* $[Alc]^{-1}$ (Fig. 2) ($r = 0.97$; $s = 55.5$) shows an intercept on the *y*-axis indicating a Michaelis–Menten dependence on the concentration of alcohol. Same fractional order dependence on the concentration of alcohol is observed for the other primary and secondary alcohols studied. The kinetic order in TsOH used for catalysing the conversion, appears to be fractional, approaching zero at high acid concentrations (Fig. 3). Initial slope of *ca* 0.47 becomes virtually zero for acid concentrations higher than *ca* $2 \cdot 10^{-2}$ mol dm^{-3}. The same trend is observed in the oxidation of isopropyl alcohol with QFC. The kinetic results are summarised in Table I.

Permittivity (*D*) values are approximately calculated from the values for pure solvents. The change of permittivity of the medium was affected by

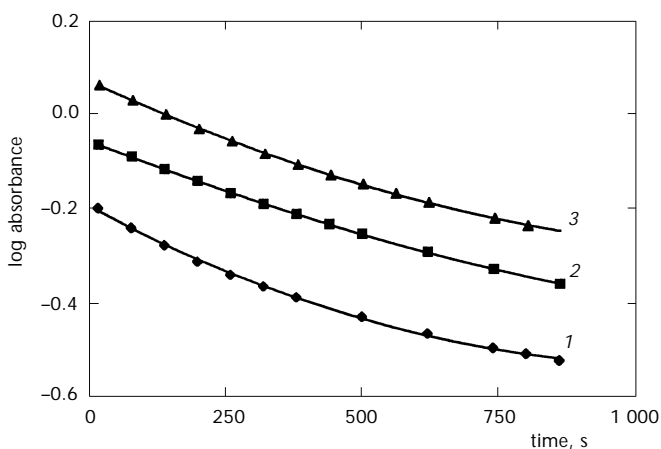FIG. 1
Time plots of logarithms of absorbance for the oxidation of methanol with quinolinium fluorochromate (QFC) in acetonitrile medium. 10^2 [MeOH] = 10.80 mol dm^{-3}, 10^3 [TsOH] = 7.53 mol dm^{-3}; *1* 10^4 [QFC] = 4.76 mol dm^{-3}, *2* 10^4 [QFC] = 6.98 mol dm^{-3}, *3* 10^4 [QFC] = 9.52 mol dm^{-3}

addition of dioxane. A small change in the D (37.50 → 33.99) of the medium enhances the rate appreciably (1.09 · 10^{-3} → 8.45 · 10^{-3} s^{-1}) (Table II). It can be seen that the solvent effect on reactivity is quite significant. A plot of log k_0 *versus* D^{-1} shows curvature. Such rate enhancement in a less polar solvent would be ascribed to the facility of formation of Cr(VI) esters[19]. A complex mechanism may also be a contributing factor to this observa-
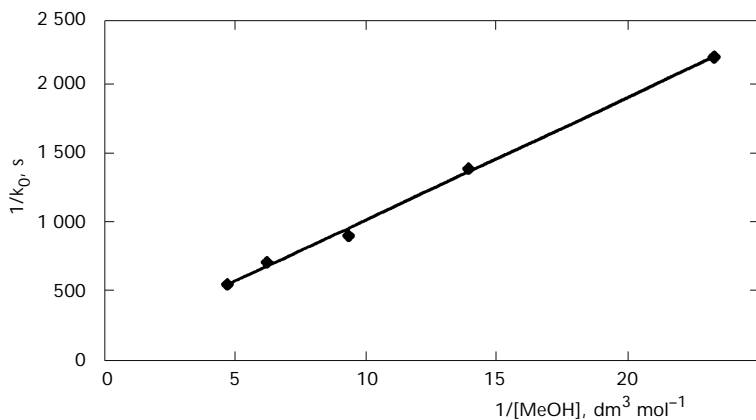

FIG. 2

The inverse–inverse plot for the reaction between methanol and quinolinium fluorochromate at 303 K. 10^3 [TsOH] = 7.53 mol dm^{-3}, 10^4 [QFC] = 4.76 mol dm^{-3}

FIG. 3

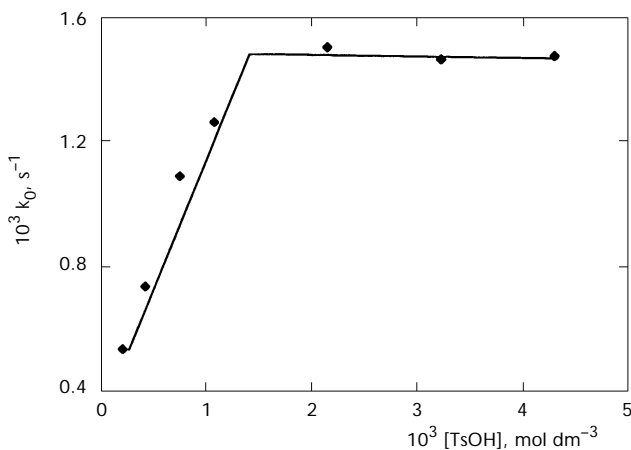A plot of k_0 *versus* [TsOH]. 10^4 [QFC] = 4.76 mol dm^{-3}, 10^2 [methanol] = 10.80 mol dm^{-3}

tion. No polymerisation with acrylonitrile is observed. Further, the rate of conversion is invariant when acrylonitrile is added. There was an appreciable change in the rate with the change in ionic strength of the medium (Table II).

We have also examined the oxidation of CD_3OD (methanol-d_4). The pseudo-first-order rate constants were derived from the initial-rate method. Kinetic behaviours are same as that of CH_3OH. The rate increases with [alcohol] with a fractional slope and the fractional order dependence on acidity approaches to zero at high acid concentrations. The kinetic data are summarised in Tables III and IV. The rate constants were measured at 293, 303 and 313 K. Activation parameters evaluated from the Eyring plots are listed in Table V. Some of the reactions were too fast to be followed spectrophoto-

TABLE I
Effect of reactants on the rate of oxidation of methanol in acetonitrile at 303 K

10^4 [QFC] mol dm^{-3}	10^2 [MeOH] mol dm^{-3}	10^3 [TsOH] mol dm^{-3}	10^3 $k_o{}^a$ s^{-1}
2.54	10.80	7.53	1.02
4.76	10.80	7.53	1.09
6.98	10.80	7.53	1.05
9.52	10.80	7.53	1.02
4.76	4.31	7.53	0.45
4.76	7.53	7.53	0.71
4.76	10.80	7.53	1.09
4.76	16.14	7.53	1.38
4.76	21.52	7.53	1.79
4.76	10.80	2.15	0.54
4.76	10.80	4.30	0.74
4.76	10.80	7.53	1.09
4.76	10.80	10.80	1.26
4.76	10.80	21.50	1.50
4.76	10.80	32.30	1.46
4.76	10.80	43.00	1.47

^{a} k_0 represents the initial rate constant.

metrically at 313 K, which led to a rough estimate of rate constants at high temperatures.

Correlation Analysis

The rate data fit reasonably well with Taft's[20] inductive σ^* values and steric substitution constants, E_s, separately.

At 303 K,

$$\log k_3 = -1.75\sigma^* - 1.25 \tag{1}$$
$$(r = 0.986;\ s = 0.076;\ n = 7)\ ,$$

where k_3 represents the rate coefficient of slow step.

TABLE II
Effect of acrylonitrile and $LiClO_4$ concentration and solvent composition on the reaction rate at 303 K

[QFC] = $4.76 \cdot 10^{-4}$ mol dm^{-3} [TsOH] = $7.53 \cdot 10^{-3}$ mol dm^{-3}
[MeOH] = $10.80 \cdot 10^{-2}$ mol dm^{-3}

10^3 [AN], mol dm^{-3}	10^4 [LiClO$_4$], mol dm^{-3}	D	$10^3\ k_o$, s^{-1}
0.0	0.0	37.50	1.09
1.43	0.0	37.50	0.91
4.30	0.0	37.50	0.91
7.17	0.0	37.50	0.94
10.04	0.0	37.50	0.92
0.0	2.57	37.50	1.00
0.0	5.14	37.50	0.83
0.0	7.71	37.50	0.72
0.0	10.27	37.50	0.67
0.0	0.0	37.50	1.09
0.0	0.0	36.79	4.46
0.0	0.0	36.09	5.87
0.0	0.0	35.39	7.47
0.0	0.0	33.99	8.45

TABLE III
Effect of oxidant, substrate and acid concentration on the reaction rate in acetonitrile at 303 K

10^4 [QFC] mol dm^{-3}	10^2 [CD$_3$OD] mol dm^{-3}	10^3 [TsOH] mol dm^{-3}	10^3 k_o s^{-1}
1.90	10.80	7.53	1.09
3.17	10.80	7.53	1.07
4.76	10.80	7.53	1.08
6.98	10.80	7.53	1.08
9.52	10.80	7.53	1.06
4.76	6.90	7.53	0.68
4.76	10.80	7.53	1.08
4.76	20.70	7.53	1.56
4.76	31.10	7.53	2.16
4.76	41.40	7.53	2.46
4.76	20.70	2.15	0.72
4.76	20.70	4.30	1.16
4.76	20.70	7.53	1.56
4.76	20.70	12.90	1.91
4.76	20.70	21.50	1.86
4.76	20.70	32.30	1.88

TABLE IV
Effect of solvent composition on the reaction rate
[QFC] = 4.76 · 10^{-4} mol dm^{-3} [TsOH] = 7.53 · 10^{-3} mol dm^{-3}
[CD$_3$OD] = 10.80 · 10^{-2} mol dm^{-3}

D	10^4 k_o, s^{-1}
37.50	1.56
37.15	28.40
36.79	43.40
36.44	51.00
36.09	58.80
34.68	71.00

$$\log k_3 = -0.674 E_s - 1.25 \qquad (2)$$
$$(r = 0.977;\ s = 0.098;\ n = 7)$$

A good correlation is also obtained with Pavelich–Taft dual substituent parameter equation[21].

$$\log k_3 = -1.67\sigma^* - 0.032 E_s - 1.253 \qquad (3)$$
$$(100R = 98.6;\ SE = 0.085;\ n = 7)$$

Few alcohols are excluded from the correlation since the corresponding substituent constants are not available. The negative polar reaction constant indicates an electron-deficient transition state. The negative steric reaction constant shows steric acceleration. Steric contributions seem to be much lower than the inductive effect.

TABLE V
Rate constants and activation parameters for the oxidation of alcohols with QFC in acetonitrile
[QFC] = $4.76 \cdot 10^{-4}$ mol dm^{-3} [TsOH] = $7.53 \cdot 10^{-3}$ mol dm^{-3}
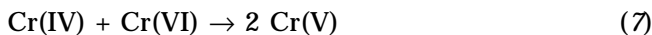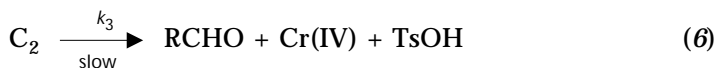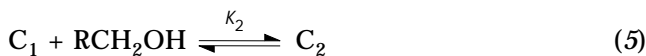
No.	Substrate	$10^3\ k_3$, s^{-1}			$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta G^{\#}$ (303K) kJ mol^{-1}	r	s
		293 K	303 K	313 K					
1	Methanol	3.78	7.22	14.44	48.6	125.6	86.6	0.999	0.039
2	Methanol-d_4	0.19	0.53	0.97	60.1	110.7	93.6	0.992	0.144
3	Ethanol	47.95	68.54	83.97	19.1	204.6	81.2	0.987	0.058
4	Propan-1-ol	60.07	87.42	109.67	20.3	198.9	80.5	0.990	0.053
5	Propan-2-ol	74.04	106.36	130.27	19.1	201.0	80.1	0.990	0.050
6	Butan-1-ol	70.79	94.77	130.86	21.0	195.5	80.2	0.999	0.021
7	2-Methyl-propan-1-ol	64.57	88.34	111.39	18.3	205.0	80.5	0.997	0.026
8	Butan-2-ol	111.79	131.13	154.97	9.9	229.3	79.4	0.998	0.012
9	Pentan-1-ol	73.71	99.87	127.22	18.3	204.0	80.1	0.999	0.017
10	Pentan-2-ol	119.74	140.60	162.05	8.8	232.6	79.3	0.999	0.001
11	Hexan-1-ol	69.27	96.56	125.36	20.3	197.9	80.2	0.998	0.021
12	Heptan-1-ol	74.50	102.98	128.41	18.4	203.8	80.1	0.995	0.034

MECHANISM

UV-VIS spectrum (Fig. 4) clearly confirms the complex formation between oxidant and TsOH. Complex formation between imidazolium dichromate–TsOH (ref.[22]) and pyridinium dichromate–TsOH (ref.[23]) has already been reported. Also specific acid catalysis by TsOH gives supporting evidence for the complex formation. QFC–TsOH complex is more reactive than Cr(VI) species since the complexation makes the oxidant a better electrophile. It behaves like a protonated Cr(VI) species which is a stronger oxidant and electrophile. Formation of a protonated Cr(VI) species has earlier been postulated in the reaction of QFC with α-hydroxy acids in perchloric acid medium[24]. The Michaelis–Menten dependence on [Alc] implies that complex formation[25] beween the alcohol and oxidant/oxidant–TsOH complex takes place in the present experiments. The kinetic order in the acid, changing from fractional to zero and yielding a limiting k_0^{max} value at high acidities, could be described by the following scheme.

$$
\text{TsOH} + \quad
\begin{array}{c}
\text{O} \quad\quad \text{O}^-\text{QH}^+ \\
\diagdown \quad\diagup \\
\text{Cr} \\
\diagup \quad\diagdown \\
\text{O} \quad\quad \text{F}
\end{array}
\quad \underset{K_1}{\rightleftharpoons} \quad
\begin{array}{c}
\text{TsO}\cdots\text{H}\cdots\text{O} \quad\quad \text{O}^-\text{QH}^+ \\
\diagdown \quad\diagup \\
\text{Cr} \\
\diagup \quad\diagdown \\
\text{O} \quad\quad \text{F}
\end{array}
\tag{4}
$$

$$(C_1)$$

$$C_1 + RCH_2OH \underset{}{\overset{K_2}{\rightleftharpoons}} C_2 \tag{5}$$

$$C_2 \underset{slow}{\overset{k_3}{\longrightarrow}} RCHO + Cr(IV) + TsOH \tag{6}$$

$$Cr(IV) + Cr(VI) \rightarrow 2\ Cr(V) \tag{7}$$

$$2\ Cr(V) + 2\ RCH_2OH \rightarrow 2\ RCHO + 4\ H^+ + 2\ Cr(III) \tag{8}$$
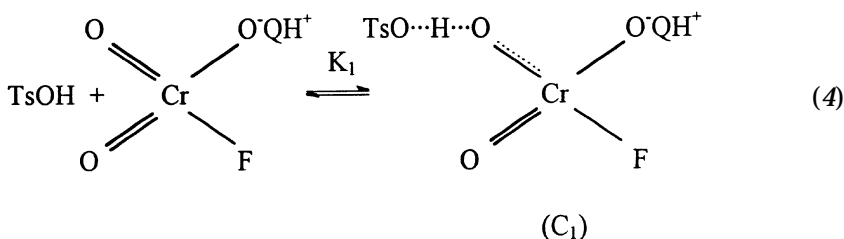
$$(Rate)_0 = k_3[C_2] \tag{9}$$

$$[QFC]_t = [QFC] + [C_1] + [C_2] \tag{10}$$

The steady-state treatment is applied and the $[C_1]$ and $[C_2]$ values are substituted.

$$(\text{Rate})_0 = \frac{k_3 K_1 K_2 [\text{Alc}][\text{TsOH}][QFC]_t}{1 + K_1 [\text{TsOH}] + K_1 K_2 [\text{Alc}][\text{TsOH}]} \tag{11}$$

$$(\text{Rate})_0 = \frac{k_3 K_1 K_2 [\text{Alc}][\text{TsOH}][QFC]_t}{1 + [\text{TsOH}](K_1 + K_1 K_2 [\text{Alc}])} \tag{12}$$
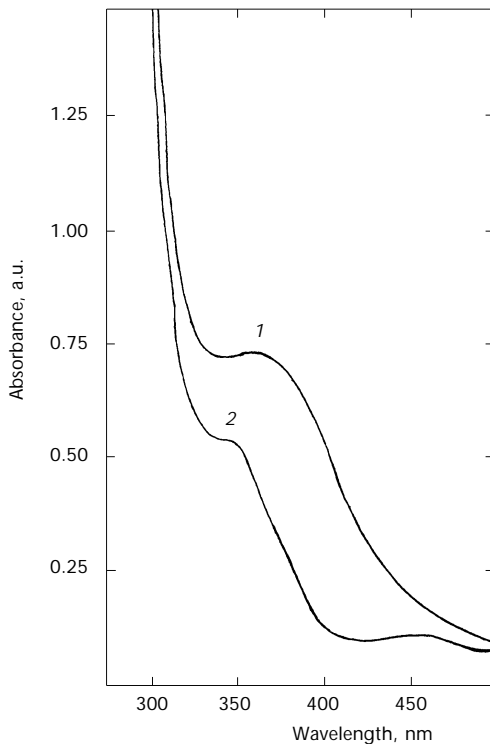

FIG. 4
UV-VIS spectra of QFC in acetonitrile. *1* QFC, *2* QFC with TsOH

The derived rate expression explains the reactivity dependence on acidity. At higher [TsOH], the factor of unity in the denominator can be neglected in comparison with the other term.

$$(\text{Rate})_0 = \frac{k'[\text{Alc}][\text{TsOH}][\text{QFC}]_t}{[\text{TsOH}](K_1 + K_1 K_2 [\text{Alc}])} \,, \tag{13}$$

where $k' = k_3 K_1 K_2$.

$$(\text{Rate})_0 = \frac{k'[\text{Alc}][\text{QFC}]_t}{K_1 + K_1 K_2 [\text{Alc}]} \tag{14}$$

This rate law explains the zero-order dependence on acidity at high concentrations of TsOH. The rate equation (*12*) can be rearranged.

$$\frac{1}{k_0} = \frac{1}{k_3 K_1 K_2 [\text{Alc}][\text{TsOH}]} + \frac{1}{k_3 K_2 [\text{Alc}]} + \frac{1}{k_3} \tag{15}$$

$$\frac{1}{k_0} = \frac{1}{[\text{Alc}]} \left\{ \frac{1}{k_3 K_1 K_2 [\text{TsOH}]} + \frac{1}{k_3 K_2} \right\} + \frac{1}{k_3} \tag{16}$$

From the double reciprocal plot of $1/k_0$ *versus* $1/[\text{Alc}]$ at constant [TsOH] (Fig. 2) ($r = 0.997$; $s = 55.5$), the rate coefficients for the slow step, k_3, can be determined. Substrate effect studies were extended to all the alcohols at different temperatures and k_3 (s^{-1}) values are listed in Table V.
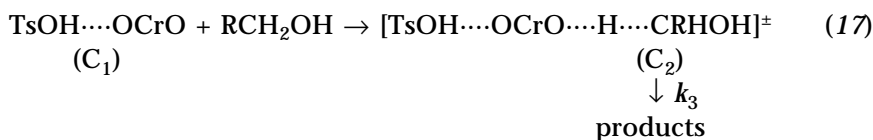
The exact nature of the Cr(IV) species is not known. Formation of Cr(IV)–TsOH and Cr(V)–TsOH complexes in the course of the reaction is not ruled out. Invariance of rate with the added acrylonitrile rules out a hydrogen abstraction mechanism. Further, ρ* values (*ca* –1.6) are not in agreement with a radical process. Generally, radical processes are characterised by small ρ values[26,27]. Studies on CD$_3$OD oxidation give some idea about the nature of the electron-deficient transition state. Significant primary isotope effects were found for CH$_3$OH ($k_0^H / k_0^D > 10$) upon deuterium substitution in all the C–H bonds. Isotope effects for some reactions that proceed by hydride mechanisms are listed in Table VI.

The large primary kinetic isotope effect in this study strongly favours a hydride transfer mechanism. The ρ values higher than –3 generally suggest a fairly large degree of carbonium character in the transition state[31]. The ρ* value of *ca* –1.6 in the present study is indicative of a partial bonding. A lin-

ear transition state will certainly exhibits a larger isotope effect than a cyclic intermediate[32]. Hence the probable structure of C_2 will be

$$[TsOH\cdots OCrO\cdots H\cdots CRHOH] .$$
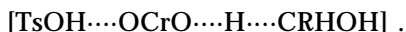
We propose a concerted, two-electron hydride transfer mechanism. This mechanism is very similar to that proposed in the oxidation of alcohols by the aquachromium(IV) ion[32].

$$TsOH\cdots OCrO + RCH_2OH \rightarrow [TsOH\cdots OCrO\cdots H\cdots CRHOH]^{\pm} \quad (17)$$
$$(C_1) \qquad\qquad\qquad\qquad (C_2)$$
$$\downarrow k_3$$
$$products$$

Nearly constant $\Delta G^{\#}$ values imply that a common mechanism operates in all the alcohols listed. There is a linear relationship between $\Delta H^{\#}$ and $\Delta S^{\#}$ ($r = 0.995$; $s = 1.57$). The excellent linearity observed in the Exner plot (Fig. 5) ($r = 0.992$; $s = 0.050$) further confirms the above view.

Comparison with Structurally Similar Oxidants

Quinolinium fluorochromate was found to undergo a concerted non-cyclic two-electron hydride transfer mechanism with alcohols in acetonitrile medium whereas the available literature on pyridinium fluorochromate[25] oxidation of ethanol in acetonitrile–nitrobenzene medium shows that the reaction follows a hydride transfer mechanism *via* the formation of a chromate ester, similar to oxidations involving chromic acid[33].

TABLE VI
Isotope effects for alcohol oxidation

Oxidant	Deuterium substitution	k_o^H/k_o^D	Reference
$[RuO(bpy)(py)]^{2+}$	CH_3OH/CD_3OH	9	28, 29
	$C_6H_5CH_2OH/C_6H_5CD_2OH$	50	28, 29
RuO_4	$(CH_3)_2CHOH/(CH_3)_2CDOH$	4.6	30

The results of the oxidation of benzyl alcohols with QCC (ref.[34]) in a DMSO–CH$_2$Cl$_2$ solution reveal that hydrogen transfer does not take place by a non-cyclic bimolecular process. A transition state having a planar, cyclic symmetrical structure is envisaged.
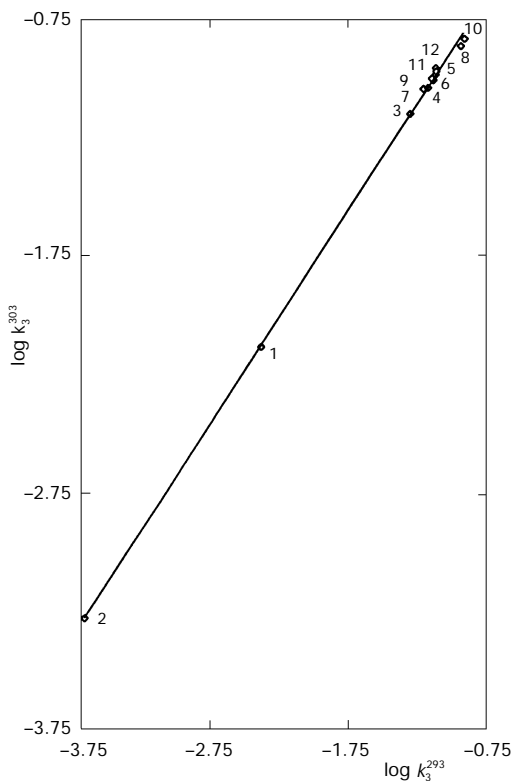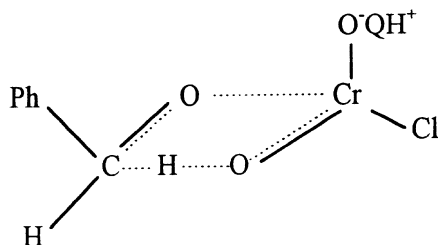

FIG. 5
The Exner plot (for numbering see Table V). 10^3 [TsOH] = 7.53 mol dm^{-3}, 10^4 [QFC] = 4.76 mol dm^{-3}

Detailed kinetic studies on the oxidation of alcohols with QFC indicate that the oxidation with QFC and PFC (ref.[25]) follow different mechanistic pathways.

Oxidation of Unsaturated Alcohols

Oxidation studies were carried out under pseudo-first-order conditions and the first-order rate coefficients were determined as explained before. There was no significant oxidation in the absence of TsOH. The reaction order dependent on acidity ranges from 1 to 2 ($r > 0.977$; $s < 0.052$). A Michaelis–Menten dependence on [Alc] is observed ($r > 0.993$; $s < 15.34$). The kinetic data are summarised in Table VII.

TABLE VII
Pseudo-first-order rate constants for variation of [TsOH], [QFC] and [Alc] in acetonitrile at 303 K

10^3 [TsOH] mol dm^{-3}	10^4 [QFC] mol dm^{-3}	10^3 [Alc] mol dm^{-3}	$10^3\ k_o$, s^{-1}		
			allyl alcohol	but-2-en-1-ol	cinnamyl alcohol
2.80	4.16	16.95	5.38	5.04	6.29
2.80	5.56	16.95	1.84	4.12	3.41
2.80	8.34	16.95	1.16	1.74	1.87
2.80	5.56	5.65	0.77	2.16	1.85
2.80	5.56	11.30	1.58	3.28	2.86
2.80	5.56	16.95	1.84	4.12	3.41
2.80	5.56	22.60	2.26	5.01	3.92
2.80	5.56	28.25	3.05	5.31	4.18
1.87	5.56	16.95	1.16	2.40	1.71
2.24	5.56	16.95	1.44	3.30	2.82
2.80	5.56	16.95	1.84	4.12	3.41
3.70	5.56	16.95	2.96	6.46	5.11
4.48	5.56	16.95	4.07	–	–

Ionic strength has no appreciable effect on the reactivity (Table VIII). A decrease in the permittivity of the medium increases the oxidation rate marginally. Added quinoline depresses the reactivity significantly as shown in Table VIII. The rate constants were measured at 283, 293, 303 and 313 K; the activation parameters are listed in Table IX.

TABLE VIII

Dependence of the rate of allyl alcohol oxidation on [AN], solvent composition, [LiClO$_4$] and [quinoline] at 303 K

[QFC] = $5.56 \cdot 10^{-4}$ mol dm^{-3} 　　　　　　　　　　　　[TsOH] = $2.80 \cdot 10^{-3}$ mol dm^{-3}

[allyl alcohol] = $16.95 \cdot 10^{-3}$ mol dm^{-3}

10^3 [AN] mol dm^{-3}	D^a	10^4 [LiClO$_4$] mol dm^{-3}	10^5 [Quinoline] mol dm^{-3}	$10^3 k_o$, s^{-1}
0.0	37.50	0.0	0.0	1.84
0.63	37.50	0.0	0.0	2.23
1.26	37.50	0.0	0.0	2.11
1.89	37.50	0.0	0.0	2.17
0.0	37.50	0.0	0.0	1.84
0.0	35.74	0.0	0.0	2.15
0.0	33.97	0.0	0.0	2.16
0.0	32.21	0.0	0.0	1.96
0.0	30.44	0.0	0.0	2.08
0.0	37.50	0.73	0.0	1.78
0.0	37.50	1.45	0.0	1.72
0.0	37.50	2.18	0.0	1.68
0.0	37.50	2.90	0.0	1.58
0.0	37.50	0.0	3.49	1.78
0.0	37.50	0.0	6.98	1.65
0.0	37.50	0.0	10.46	1.28
0.0	37.50	0.0	17.44	1.21

^{a} Permittivity values are calculated from the values for pure solvents.

The rate constants decreased with increasing [QFC]. This observation is very common in Cr(VI) oxidations. The oxidant must be in equilibrium with a less reactive species. This behaviour in aqueous solution is well explained by Wiberg[35]. The rate is dependent on the concentration of acid chromate ion rather than on total Cr(VI).

$$2 \; HCrO_4^- \; \rightleftharpoons \; Cr_2O_7^{2-} \; + \; H_2O \qquad (18)$$
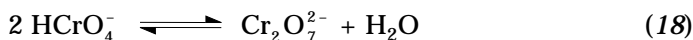
Thus, as the concentration of chromium(VI) is increased, a progressively decreasing portion of the total amount is in the form of the acid chromate ion and the rate constants decrease with increasing chromium(VI) concentration. In acetonitrile medium, the formation of [QFC–acetonitrile] adduct can be envisaged. This decreases the effective concentration of QFC and, as a result, the reactivity decreases. If the formation constant of the adduct is insignificant, then inverse dependence of the rate on [oxidant] will not be observed. A shift in λ_{max} from 360 nm in aqueous medium to 360–370 nm in acetonitrile medium is observed. A similar shift in λ_{max} is more pronounced in Cr(V) complexes (510 nm in aqueous medium to 540 nm in acetonitrile medium)[36,37]. The kinetic data can be described by a two mechanisms.

TABLE IX
Rate constants and activation parameters for the oxidation of allyl alcohol, cinnamyl alcohol and but-2-en-1-ol with QFC in acetonitrile
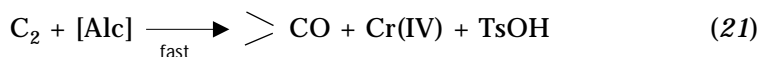[QFC] = $5.56 \cdot 10^{-4}$ mol dm^{-3} [TsOH] = $2.80 \cdot 10^{-3}$ mol dm^{-3}

No	Substrate	$10^2 \, k^a$				$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta G^{\#}$ (303K) kJ mol^{-1}	r	s
		283 K	293 K	303 K	313 K					
1	Allyl alcohol	2.18	3.25	4.43	7.57	27.2	180.5	81.9	0.990	0.083
2	Cinnamyl alcohol	4.88	9.58	14.33	26.44	37.7	136.2	79.0	0.996	0.076
3	But-2-en-1-ol	1.78	2.56	4.03	6.59	29.5	174.3	82.3	0.994	0.070

^{a} $k = k_0 /[Alc]^n$, where n is the reaction order with respect to alcohols.

$$OX + TsOH \xrightleftharpoons{K_1} C_1 \tag{19}$$

$$C_1 + TsOH \xrightleftharpoons{K_2} C_2 \tag{20}$$
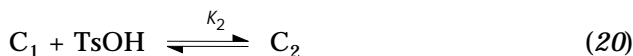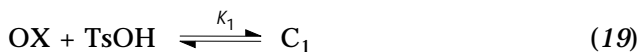
(the forward reaction is rate-determining)

$$C_2 + [Alc] \xrightarrow[fast]{} {>} CO + Cr(IV) + TsOH \tag{21}$$

SCHEME 1

C_2 is similar to an activated complex containing two substrate molecules[38–46].

$$OX + TsOH \xrightleftharpoons{K_1} C_1 \tag{19}$$

$$C_1 + [Alc] \xrightleftharpoons[slow]{K_3} C_3 \tag{22}$$

$$C_3 \xrightarrow[slow]{k_4} products \tag{23}$$
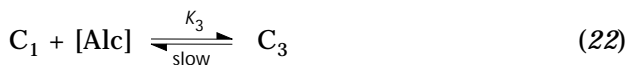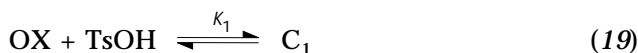
SCHEME 2

The overall rate is

$$(Rate)_0 = \frac{k_2 K_1 [TsOH]^2 [QFC]_t}{1 + K_1 [TsOH]} + \frac{k_4 K_1 K_3 [Alc][TsOH][QFC]_t}{1 + K_1 [TsOH]} . \tag{24}$$

At low [TsOH],

$$k_0 = k_2 K_1 [TsOH]^2 + k_4 K_1 K_3 [Alc][TsOH] \tag{25}$$

$$\frac{k_0}{[\text{TsOH}]} = k_2 K_1 [\text{TsOH}] + k_4 K_1 K_3 [\text{Alc}] \ . \tag{26}$$

The plot of $k_0/[\text{TsOH}]$ *versus* [TsOH] is reasonably linear (Fig. 6) ($r = 0.976$; $s = 0.031$) with an intercept thus proving the validity of the assumptions.

Product analysis shows that propenal, but-2-enal and cinnamaldehyde are the main products. This rules out the possibility of attack of oxidising species on the double bond of these alcohols. Nearly constant $\Delta G^{\#}$ values imply the operation of a common mechanism with all the alcohols. The linear relation in the Exner plots ($r > 0.992$; $s < 0.054$) further confirms the above view. The order of reactivity is, cinnamyl alcohol > allyl alcohol > but-2-en-1-ol. A reverse order of reactivity is exhibited in the oxidation of alcohols with selenium dioxide[47]. Close observation of the rate coefficients of allyl alcohol and but-2-en-1-ol indicates that their reactivities are almost same. This is quite expected, since the methyl group is isolated from the reaction centre by the C=C bond. The +I effect of the methyl group is not significant in this system. The high reactivity of cinnamyl alcohol can be ascribed to resonance interaction through the conjugated double bonds.
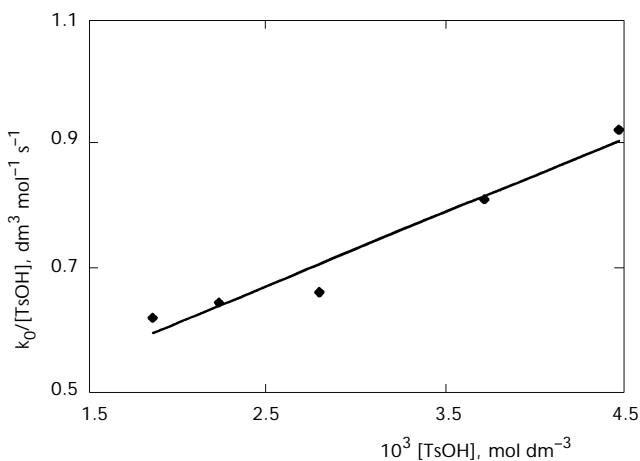

Fig. 6
A plot of $k_0/[\text{TsOH}]$ *versus* [TsOH]. 10^4 [QFC] = 5.56 mol dm^{-3}, 10^3 [allyl alcohol] = 16.95 mol dm^{-3}

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