



KINETICS AND MECHANISM OF OXIDATION OF SECONDARY ALCOHOLS BY MORPHOLINIUM FLUOROCHROMATE

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Oxidation of several secondary alcohols by morpholinium fluorochromate (MFC) in DMSO leads to the formation of corresponding ketones. The reaction is first order each in MFC and acidity. The reaction exhibited Michaelis-Menten kinetics with respect to alcohols. The oxidation of 2-propanol-*d*₂ (MeCDOHMe) exhibited a substantial primary kinetic isotope effect ($k_H/k_D = 5.16$ at 298 K). The oxidation of 2-propanol has been studied in nineteen different organic solvents. The solvent effect has been analysed using Taft's and Swain's multiparametric equations. The reaction was subject to both polar and steric effects of the substituents. A mechanism involving transfer of hydride ion from alcohol to the oxidant, via a chromate ester, has been proposed.

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INTRODUCTION

Chromium (VI) is a versatile oxidant but is a rather drastic and non-selective oxidant. To improve the selectivity of Cr (VI), a number of organic halochromates have been synthesized used as mild and selective oxidizing reagents in synthetic organic chemistry.¹⁻⁵ Morpholinium fluorochromate (MFC) is one such compound used for the oxidation of aryl alcohols.⁶ Some reports on the kinetic aspects of oxidation by MFC, including that on the oxidation of primary alcohols, has appeared recently,⁷ however, there seems to be no report on the oxidation of secondary alcohols by MFC. It is known, however, that primary and secondary organic compounds sometimes follow different mechanistic pathways.⁸ We now report the kinetics and mechanism of oxidation of ten secondary alcohols by MFC in DMSO as a solvent. The mechanistic aspects have been discussed.

EXPERIMENTAL

Materials

All the alcohols were commercial products (Fluka) and the liquid alcohols were dried over anhydrous magnesium sulphate and then fractionated. Benzhydrol was recrystallised from ethanol. MFC was prepared by the reported method⁶ and its purity was checked by an iodometric method. 2-Propanol-2*d*₁ (MeCDOHMe, D-2-Pr), of 98 % atom D, was obtained from Sigma-Aldrich. Due to the non-aqueous nature of the solvents, p-toluenesulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by the usual methods.⁹

Product Analysis

The product analysis was carried out under kinetic conditions, i.e., with an excess of the alcohol over MFC. In a typical experiment, 2-propanol (0.05 mol), TsOH (0.005 mol) and MFC (2.07 g, 0.01 mol) were made up to 100 mL in DMSO and the reaction mixture was kept in dark for ≈ 10 h to ensure completion of the reaction. The solution was then treated with excess (200 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 2.16 g (91 %) and 2.05 g (86 %) respectively, based on the consumption of MFC. The DNP was found to be identical (m.p. and mixed m.p.) with the DNP of acetone.

In similar experiments, with other alcohols, the yield of the DNP was in the range of 77-87 % after recrystallization. The oxidation state of chromium in completely reduced reaction mixture, determined by iodometric titrations, was 3.90 ± 0.15 .

Kinetic Measurements

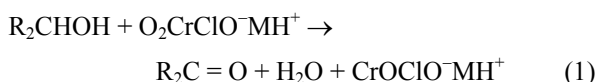
Reactions were carried out under pseudo-first-order conditions by keeping an excess ($\times 15$ or greater) of the alcohol over MFC. The solvent was DMSO, unless mentioned otherwise. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions.

The reactions were carried out at constant temperature (± 0.1 K) and were followed up to 80 % of the extent of reaction, by monitoring the decrease in the concentration MFC spectrophotometrically at 356 nm. The pseudo-first-order rate constant, k_{obs} , was computed from the linear least-squares plot of $\log [MFC]$ versus time. Duplicate runs showed that the rate constants were reproducible to within ± 3 %.

RESULTS

The kinetic and other data were obtained for all the alcohols under study. As the results are similar, only representative data are reproduced here.

The oxidation of alcohols by MFC leads to the formation of corresponding ketones. The overall reaction may be written as eqn. 1 (here M = morpholine).



MFC undergoes a two-electron change. This is accord with the earlier observations with other halochromates. It has already been shown that both pyridinium chlorochromate¹⁰ and pyridinium fluorochromate (PFC)¹¹ act as two-electron oxidants and are reduced to chromium (IV) species. The oxidation state of the spent chromium species is shown to be four by determining its oxidation state by magnetic susceptibility, ESR and IR studies.^{10,11}

Rate Laws

The reactions are of first order with respect to MFC. Further, the pseudo-first-order rate constant, k_{obs} , is independent of the initial concentration of MFC. The reaction rate increases linearly with an increase in the acidity of the solution (Table 1). The reaction rate increases with increase in the concentration of the alcohol but not linearly (Table 1). A plot of $1/k_{\text{obs}}$ against $1/[\text{alcohol}]$ is linear ($r > 0.995$) with an intercept on the rate-ordinate. Thus, Michaelis-Menten type kinetics are observed with respect to the alcohol. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).



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

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. 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).

Test for Free Radicals

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 (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. This indicates that a one-electron oxidation, giving rise to free radicals, is highly unlikely in the present reaction.

Kinetic Isotope Effect

Table 1. Rate constants for the oxidation of 2-propanol by MFC at 298 K.

$10^3[\text{MFC}]$ mol dm ⁻¹	[Alcohol] mol dm ⁻³	[H ⁺] mol dm ⁻³	$10^4 k_{\text{obs}}$ s ⁻¹
1.0	0.02	0.1	2.01
1.0	0.03	0.1	2.90
1.0	0.04	0.1	3.81
1.0	0.08	0.1	6.96
1.0	0.12	0.1	9.62
1.0	0.20	0.1	13.7
1.0	0.25	0.1	16.1
2.0	0.20	0.1	13.3
3.0	0.20	0.1	13.9
5.0	0.20	0.1	13.6
8.0	0.20	0.1	13.5
1.0	0.20	0.2	27.0
1.0	0.20	0.3	41.1
1.0	0.20	0.5	68.6
1.0	0.20	0.7	95.2
1.0	0.20	1.0	135
1.0	0.20	0.1	13.8*

*contained 0.001 mol dm⁻¹ acrylonitrile

To ascertain the importance of the cleavage of α -C-H bond in the rate-determining step, the oxidation of 2-propanol-2-*d*₁ (MeCDOHMe, D-2-Pr) was studied. The oxidation of D-2-Pr showed that the formation constant, K , is not appreciably affected by isotopic substitution but the rate constant of the decomposition of the intermediate, k_2 , exhibited a substantial primary kinetic isotope effect (Tables 2 and 3).

Effect of Solvents

The oxidation of 2-propanol was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of MFC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics was similar in all the solvents. The values K and k_2 at 308 K are recorded in Table 4.

DISCUSSION

The correlation between activation enthalpies and entropies of the oxidation of the ten secondary alcohols is not satisfactory ($r^2 = 0.9122$), indicating that the compensation effect in this reaction is not operative in this reaction.¹² It is known, however, that the correlations between the activation enthalpies and entropies are often vitiated by the experimental errors inherent in their values. However, the oxidation of the ten secondary alcohols exhibited a good correlation in terms of Exner's equation

Table 2. Formation constants and thermodynamic parameters of the formation of MFC-alcohol (RCHOHMe) intermediate.

R	K				ΔH kJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹	ΔG kJ mol ⁻¹
	288 K	298 K	308 K	318 K			
Me	3.24	2.52	1.94	1.56	-21.2±0.2	-56±1	-4.77±0.6
Et	5.01	3.95	3.10	2.41	-21.0±0.4	-51±2	-4.87±0.3
Pr	5.49	4.18	3.70	2.62	-20.3±0.7	-48±3	-6.12±0.6
i-Pr	5.55	4.41	3.40	2.60	-21.8±0.6	-53±2	-6.12±0.6
i-Bu	2.13	1.66	1.32	1.03	-21.0±0.2	-58±1	-3.74±0.2
Bu	2.66	1.99	1.60	1.25	-21.4±0.4	-58±2	-4.25±0.3
ClCH ₂	3.02	2.30	1.74	1.35	-23.0±0.3	-62±2	-4.53±0.2
MeOCH ₂	2.95	2.19	1.75	1.40	-21.3±0.4	-57±2	-4.50±0.3
Ph	5.95	4.56	3.56	2.81	-21.5±0.4	-52±1	-6.25±0.3
Benzhydrol	3.02	2.25	1.67	1.20	-27.3±0.6	-77±3	-4.45±0.6
D-2-Pr	3.29	2.48	2.00	1.45	-22.8±0.6	-61±3	-4.77±0.6

Table 3. Rate constants and activation parameters of the decomposition of the MFC-alcohol (RCHOHMe) intermediate.

R	10 ⁴ k ₂ s ⁻¹				ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	ΔG^\ddagger kJ mol ⁻¹
	288 K	298 K	308 K	318 K			
Me	19.7	41.1	85.7	178	53.3±0.7	-112±3	86.6±0.6
Et	33.4	68.7	143	277	51.4±0.4	-114±2	85.3±0.4
Pr	58.3	108	223	400	47.0±0.7	-125±3	84.1±0.6
i-Pr	94.5	170	331	567	43.5±0.8	-133±3	83.0±0.6
i-Bu	155	262	467	749	37.9±0.6	-149±2	82.0±0.5
Bu	65.5	125	241	530	55.1±0.8	-113±3	83.8±0.7
ClCH ₂	0.40	1.10	2.57	5.94	65.6±0.7	-101±2	95.7±0.5
MeOCH ₂	3.34	7.36	16.7	36.3	58.2±0.8	-110±3	90.1±0.6
Ph	151	292	530	970	44.5±0.4	-126±1	81.8±0.3
Benzhydrol	160	300	540	970	43.1±0.5	-130±2	81.7±0.3
D-2-Pr	3.42	7.95	18.0	40.9	58.0±0.4	-109±3	90.4±0.4
k _H /k _D	5.76	5.16	4.76	4.35			

Table 4. Effect of solvents on the oxidation of 2-propanol by MFC at 308 K.

Solvent	K	10 ⁴ k ₂ , s ⁻¹	Solvent	K	10 ⁴ k ₂ , s ⁻¹
Chloroform	2.04	33.6	Acetic acid	2.13	18.1
1,2-Dichloroethane	1.98	32.1	Cyclohexane	1.68	1.27
Dichloromethane	1.86	33.0	Toluene	1.89	8.21
DMSO	1.94	85.7	MeCOPh	2.11	34.6
Acetone	2.03	27.6	THF	1.83	13.4
DMF	2.12	46.4	t-Butyl alcohol	2.04	17.5
Butanone	2.09	20.5	1,4-Dioxane	2.15	14.0
Nitrobenzene	1.92	36.0	1,2-Dimethoxyethane	1.89	8.92
Benzene	1.97	9.84	Carbon disulfide	2.04	4.35
Ethyl acetate	2.03	12.3			

of isokinetic relation.¹³ An Exner's plot between log k₂ at 288 K and at 318 K was linear (r² = 0.9990). The value of isokinetic temperature evaluated from the Exner's plot is 730±73 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.

The formation constant, K, does not show any substantial variation with the nature of the solvent (Table 4), however, the rate constant of the decomposition, k₂, of the intermediate vary with the solvent. The rate constants of the

decomposition, k₂, was therefore subjected to correlation analysis.

The rate constant, k₂, in eighteen solvents (CS₂ was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (LESR) of Kamlet and Taft (eqn. 5).¹⁴

$$\log k_2 = \rho\pi^* + b\beta + \alpha\alpha + A_0 \quad (5)$$

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, 12 have a value of zero for α . The results of correlation analyses in terms of eqn. (5), a biparametric equation involving π^* and β , and separately with π^* and β are given below as equations (6) - (9). Here n is the number of data points and ψ the Exner's statistical parameter.¹⁵

$$\log k_2 = 1.56(\pm 0.16) \pi^* + 0.13(\pm 0.13) \beta + 0.29(\pm 0.12) \alpha - 3.83 \quad (6)$$

$$R^2 = 0.8898, sd = 0.15, n = 18, \psi = 0.36$$

$$\log k_2 = 1.45 (\pm 0.17) \pi^* + 0.23 (\pm 0.40) \beta - 3.76 \quad (7)$$

$$R^2 = 0.8466, sd = 0.17, n = 18, \psi = 0.42$$

$$\log k_2 = 1.51 (\pm 0.18) \pi^* - 3.72 \quad (8)$$

$$r^2 = 0.8207, sd = 0.17, n = 18, \psi = 0.44$$

$$\log k_2 = 0.49 (\pm 0.32) \beta - 2.91 \quad (9)$$

$$r^2 = 0.1258, sd = 0.38, n = 18, \psi = 1.09$$

Kamlet's¹⁴ LESR explains *ca.* 89 % of the effect of solvent on the oxidation. However, by Exner's criterion¹⁵ the correlation is not even satisfactory (cf. eqn. 6). The major contribution is of solvent polarity. It alone accounted for *ca.* 82 % of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's¹⁶ equation (10) of cation- and anion-solvation concept 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 eqn. (10), separately with A and B and with ($A + B$).

$$\log k_2 = 1.17 (\pm 0.02) A + 1.43 (\pm 0.01) B - 4.14 \quad (11)$$

$$R^2 = 0.9996, sd = 0.01, n = 19, \psi = 0.01$$

$$\log k_2 = 0.97 (\pm 0.47) A - 3.03 \quad (12)$$

$$r^2 = 0.2010, sd = 0.28, n = 19, \psi = 0.97$$

$$\log k_2 = 1.34 (\pm 0.20) B - 3.63 \quad (13)$$

$$r^2 = 0.7091, sd = 0.23, n = 19, \psi = 0.55$$

$$\log k_2 = 1.35 \pm 0.03 (A + B) - 4.01 \quad (14)$$

$$r^2 = 0.9899, sd = 0.04, n = 19, \psi = 0.10$$

The rates of oxidation of 2-propanol in different solvents showed an excellent correlation in Swain's equation (cf. eqn. 11) with cation- and anion-solvating powers playing the important roles, though the contribution of the cation-solvation is somewhat more. In fact, the cation-solvation alone account for *ca.* 71 % of the data. The correlation with the anion-solvating power alone was very poor. The solvent polarity, represented by ($A + B$), also accounted for *ca.* 99 % of the data. Since solvent polarity accounted for 99 % of the data, attempt was made to correlate the rate constant with relative permittivity (RM). However, correlation with the inverse of RM was poor (eqn. 15).

$$\log k_2 = 1.60 \pm 0.26(1/RM) - 2.40 \quad (15)$$

$$r^2 = 0.6139, sd = 0.61, n = 19, \psi = 0.84$$

Correlation analysis of reactivity

Since the formation constant, K , of the intermediate did not exhibit much variation with the structure of the alcohol, the rate constants k_2 of the 8 aliphatic secondary alcohols were analyzed in terms of Taft's¹⁷ substituent constants.

The rate constants of oxidation of alcohols failed to yield any significant correlation separately with Taft's σ^* and E_s values.¹⁷

$$\log k_2 = -1.78 (\pm 0.16) \sum \sigma^* - 2.16 \quad (16)$$

$$r^2 = 0.9510, sd = 0.19, n = 8, \psi = 0.24, T = 298 \text{ K}$$

$$\log k_2 = -1.36 (\pm 0.99) \sum E_s - 2.81 \quad (17)$$

$$r^2 = 0.2402, sd = 0.76, n = 8, \psi = 0.93, T = 298 \text{ K}$$

The rates were, therefore, correlated in terms of Pavelich-Taft's¹⁸ dual substituent -parameter equation (eqn. 18).

$$\log k_2 = \rho^* \sum \sigma^* + \delta \sum E_s + \log k_0 \quad (18)$$

The correlations are excellent; reaction constants being negative (Table 5). There is no significant co-linearity ($r^2 = 0.2322$) between σ^* and E_s of the eight substituents.

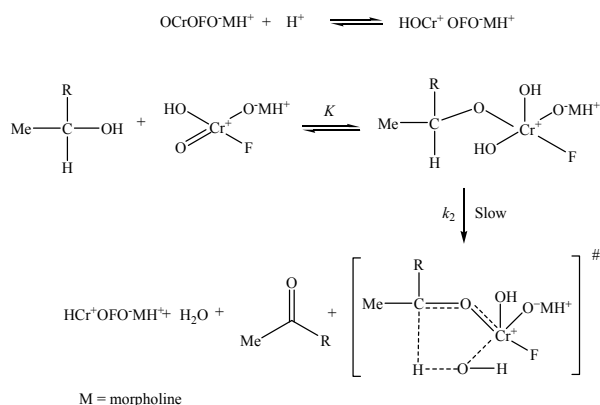
Table 5. Temperature dependence of the reaction constants.

Temp., K	ρ^*	δ	r^2	sd	ψ
288	-1.77±0.02	-0.72±0.02	0.9990	0.02	0.04
298	-1.65±0.03	-0.62±0.04	0.9985	0.03	0.05
308	-1.59±0.03	-0.57±0.04	0.9983	0.03	0.05
318	-1.53±0.03	-0.46±0.05	0.9981	0.04	0.05

The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The negative steric reaction constants points to a steric acceleration of the reaction. This may be explained on the basis of the high ground state energy of the sterically crowded alcohols.

Since the crowding is relieved in the product, ketone, as well as in the transition state leading to it, the transition state energies of the crowded and un-crowded alcohols do not differ much and steric acceleration, therefore, results. The faster oxidation of 1-phenylethanol and benzhydrol may well be due to the stabilization of the electron-deficient carbon centre in the transition state by phenyl group through resonance.

MECHANISM



Scheme 1. Mechanism of the oxidation of secondary alcohols by MFC.

The presence of a substantial primary kinetic isotope effect confirms that the α -C-H bond is cleaved in the rate-determining step. The negative value of the polar reaction constant together with the substantial deuterium isotope effect indicates the presence of an electron-deficient carbon centre in the transition state. Hence, transfer of a hydride ion from the alcohol to the oxidant is suggested. The hydride ion transfer mechanism is also supported by major role of cation-solvating power of the solvents. The hydride-ion transfer may proceed by either an acyclic bimolecular reaction or may involve a cyclic symmetrical transition state via a chromate ester. Kwart and Nickle¹⁹ 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-2-propanols, fitted to the familiar expression $k_{\text{H}}/k_{\text{D}} = A_{\text{H}}/A_{\text{D}} \exp(E_{\text{a}}/RT)$ show a direct correspondence with the properties of a symmetrical transition state^{20,21} in which the activation energy difference (E_{a}) for $k_{\text{H}}/k_{\text{D}}$ is equal to the zero-point energy difference for the respective C-H and C-D bonds (≈ 4.5 kJ/mol) and the frequency factors and the entropies of activation of the respective reactions are nearly equal. Bordwell²² has documented very cogent evidences against the occurrence of concerted one-step biomolecular processes by hydrogen transfer and it is evident that in the present studies also the hydrogen transfer does not occur by an acyclic biomolecular process. It is well-established that intrinsically concerted sigmatropic reactions, characterised by a transfer of hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer.²³ Littler²⁴ 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, a transition state having a planar,

cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. The formation of an ester intermediate is supported by the kinetic studies also. Hence, the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium step and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (Scheme 1). The observed negative value of entropy of activation also supports a polar transition state.

The solvent effect indicated that the transition state is more polarized than the reactant. Thus it is suggested the carbinol-carbon is positively polarized whereas the chromate-oxygen is negatively polarized. Similar observations have been recorded in the oxidation of organic sulphides by PFC²⁵ and methionine by pyridinium bromochromate²⁶ where a positively charged sulphur-centre and a negatively charged chromate-oxygen have been reported. In contrast, reactions involving free cations exhibited relatively much higher contribution of the cation-solvating power e.g., the oxidation of lower oxyacids of phosphorus by PFC²⁷ where the coefficient of cation-solvating power (B) is nearly five-times that the anion-solvating (A). In the oxidation of thioacids by quinolinium fluorochromate, where formation of a sulfenium cation in the rate-determining step has been suggested, the cation-solvating plays a relatively much bigger role.²⁸ The solvent effect also, thus, supports a hydride transfer reaction via a chromate ester.

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