KINETICS AND MECHANISM OF OXIDATION OF SOME THIOACIDS BY MORPHOLINIUM FLUOROCHROMATE

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Oxidation of thioglycolic, thiolactic and thiomalic acids by morpholinium fluorochromate (MFC) in dimethylsulphoxide (DMSO) leads to the formation of disulphide dimers. The reaction is first order in MFC. Michaelis-Menten type of kinetics is observed with respect to the thioacids. Reaction failed to induce the polymerisation of acrylonitrile. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has the form $k_{obs} = a + b [H^+]$. The oxidation of thiolactic acid has been studied in nineteen different organic solvents. The solvent effect has been analysed by using Kamlet's and Swain's multiparametric equations. A mechanism involving the formation of a thioester and its decomposition in slow step has been proposed.

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Introduction

Salts of Cr(VI) have long been used as oxidizing reagents in synthetic organic chemistry. However, these salts are drastic and non-selective oxidants in nature. Further, they are insoluble in most of the organic solvents also. Thus miscibility is a problem. 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.[1] One such compound is morpholinium fluorochromate (MFC).[2] Only a few reports are available in literature regarding oxidation aspects of MFC.[3-4] It is known that the mode of oxidation by Cr(VI) derivatives depends on the nature of the counter-ion attached to the chromium anion. Therefore, in continuation of our earlier work, in the present article, we report the kinetics of the oxidation thioglycolic (TGA), thiolactic (TLA) and thiomalic (TMA) acids by morpholinium fluorochromate in DMSO as solvent. Mechanistic aspects are also discussed.

Experimental

Materials

The thioacids (Fluka) and dithiodiglycolic acid (Evan Chemicals, USA) were commercial products and were used as such. Dithiodimalic and dithiodilactic acids were prepared by the oxidation of the corresponding thiols by ferric alum.[5] The method results in products with nearly 99% purity. The solutions of the thioacids were freshly prepared in DMSO and were standardized by titrating them against a standard solution of iodine.[5,6] MFC was prepared by the reported method[2] and its purity was checked by an iodometric method. The solvents were purified by usual methods.[7] p-Toluenesulphonic acid (TsOH) was used as a source of hydrogen ions.

Stoichiometry

Stoichiometric determinations, as well as the characterization of the products, carried out polarigraphically[8,9] using an automatic (Heyrovsky TP 55A) polarograph. It was found that the cathode wave given by a known sample of disulphide dimer coincided by the wave given by the final product of the oxidation. The reaction exhibited a 1:2 stoichiometry, i.e. 2 moles of the thiol are oxidized per mole of MFC reduced. Further, the reaction mixtures with an excess of MFC were allowed to go to completion and the residual MFC was determined iodometrically. These results also gave a 1:2 stoichiometry (eqn.1). The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method, is 3.95±0.10.

$$2\ RSH + O_2CrFOMH \longrightarrow RS\text{-}SR + H_2O + OCrFOMH \quad (1)$$

MFC undergoes two-electron change. This is in accordance with the earlier observations with structurally similar other halochromates also. It has already been shown that both pyridinium chlorochromate (PCC)[10] and pyridinium fluorochromate (PFC)[11] act as two-electron oxidants and are reduced to chromium (IV) species by determining the oxidation state of chromium by magnetic susceptibility, ESR and IR studies.
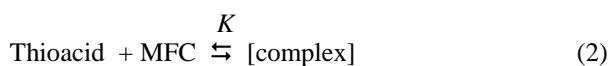
Kinetic Measurements

The reactions were carried out under pseudo-first-order conditions by keeping a large excess ($\times$ 15 or greater) of the thioacids over MFC. The solvent was DMSO, unless specified otherwise. The reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions and were followed up to ca. 80% conversion by monitoring the decrease in the [MFC] at 352 nm on a spectrophotometer (AIMIL, India, Model MK-II). The MFC showed a λ_{max} of 352 nm. Further, no other species had any noticeable absorbance at this wavelength. The pseudo-first-order rate constants, k_{obs}, were evaluated from the linear least-squares plots of log [MFC] against

time. Duplicate kinetic runs showed that the rate constants are reproducible to within ±3 %. All reactions, other than those to study the effect of [H$^+$], were performed in the absence of TsOH.

Results and Discussion

Rate-laws

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

$$\text{Thioacid} + \text{MFC} \overset{K}{\leftrightarrows} [\text{complex}] \qquad (2)$$

$$[\text{Complex}] \overset{k_2}{\rightarrow} \text{Products} \qquad (3)$$

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

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).

Table 1. Rate constants for the oxidation of thioacids by MFC at 298 K.

10^3 MFC mol dm^{-3}	[Thioacid] mol dm^{-3}	10^4 k_{obs} s^{-1}		
		TGA	TLA	TMA
1.0	0.10	4.28	21.0	10.0
1.0	0.20	6.68	32.0	15.5
1.0	0.40	9.30	43.5	21.3
1.0	0.60	10.7	49.3	24.4
1.0	0.80	11.6	52.9	26.3
1.0	1.00	12.2	55.3	27.5
1.0	1.50	13.0	58.8	29.5
1.0	3.00	14.1	62.9	31.7
2.0	0.40	9.36	45.9	21.6
4.0	0.40	9.03	44.1	20.7
6.0	0.40	9.18	45.0	22.5
8.0	0.40	9.27	44.7	21.0
1.0	0.20	6.75	33.3	16.2

Test for free radicals

The oxidation of thioacids by MFC, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate (Table 1). Thus a one electron oxidation, giving rise to free radicals, is unlikely.
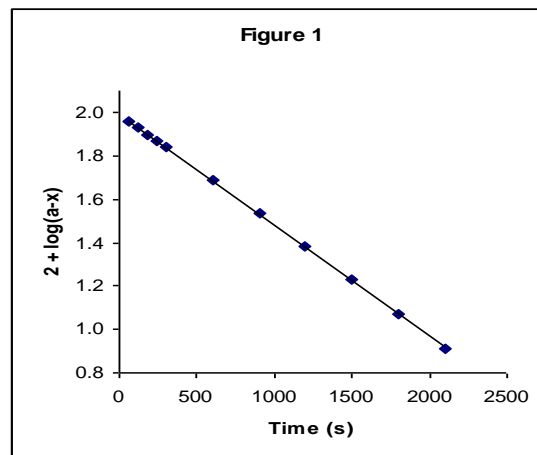

Figure 1. A typical kinetic run.

Effect of acidity

The reaction is catalysed by hydrogen ions (Table 4). The hydrogen- ion dependence has the following form $k_{obs} = a + b$ [H$^+$]. The values of a and b, for TLA, are $20.7 \pm 0.13 \times 10^{-4}$ s^{-1} and $37.6 \pm 0.21 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 =$ 0.9870). The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one is acid-independent and the other is acid-dependent. The acid-catalysis may well be attributed to a protonation of MFC to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile (5).

$$\text{O}_2\text{CrFOMH} + \text{H}^+ \overset{}{\leftrightarrows} (\text{HOCrOFOMH})^+ \qquad (5)$$
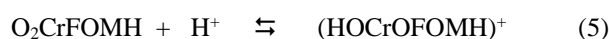
Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar halochromates.

Effect of solvents

The oxidation of thiolactic acid 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 dependence of rate on [Thioacid] and [MFC] were studied in all the solvents. The kinetics were similar in all the solvents. The formation constant of the intermediate complex, K, did not vary much (5.27 ± 0.46) with the solvent but the rate constant, k_2, exhibited much variation in values with different solvents (Table 5).

Table 2. Rate constants for the decomposition of MFC–Thioacids complexes and their activation parameters.

Thioacid	$10^3 k_2$ (dm^{-3} mol^{-1} s^{-1})				$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$
	288 K	298 K	308 K	318 K	kJ mol^{-1}	J mol^{-1}K^{-1}	kJ mol^{-1}
TGA	8.10	15.3	28.8	52.2	44.8±0.3	180± 1	83.3± 0.3
TLA	39.6	67.5	117	189	37.4±0.3	142± 1	79.7± 0.3
TMA	18.9	34.2	60.3	99.0	39.6±0.2	141± 1	81.4± 0.2

Table 3. Formation constants for the decomposition of MFC–thioacids complexes and their thermodynamic parameters.

Thioacid	K dm^3 mol^{-1}				ΔH	$-\Delta S$	ΔG
	288 K	298 K	308 K	318 K	kJ mol-1	J mol-1K-1	kJ mol-1
TGA	4.68	3.88	3.07	2.82	20.2±0.9	49±3	5.78±0.8
TLA	5.31	4.52	3.70	2.88	17.9±0.9	40±3	6.17±0.7
TMA	4.95	4.15	3.33	2.56	19.2±0.9	45±3	5.95±0.7

Table 4. Effect of hydrogen ion concentration on the oxidation of thioacids by MFC

[H$^+$] mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
TGA	4.95	6.21	7.11	8.28	10.8	11.7
TLA	24.3	28.8	36.9	40.5	52.2	58.5
TMA	11.7	13.5	17.1	19.8	25.2	27.9

[MFC] = 0.001 mol dm^{-3}, [Thioacids] = 1.0 mol dm^{-3}, Temp. = 298 K

The rate constants of the oxidation, k_2, in eighteen solvents (CS$_2$ 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[12] (6).

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \tag{6}$$

Table 5. Effect of solvents on the oxidation of TLA by MFC at 298 K.

Solvents	$10^3 k_{obs}$ s^{-1}	Solvents	$10^3 k_{obs}$ s^{-1}
CHCl$_3$	20.9	Toluene	9.77
ClCH$_2$CH$_2$Cl	27.5	PhCOMe	36.3
CH$_2$Cl$_2$	24.0	THF	14.8
DMSO	67.5	t-BuOH	10.2
Acetone	22.4	1,4-Dioxane	16.2
DMF	41.7	MeOCH$_2$CH$_2$OME	9.12
Butanone	18.2	CS$_2$	5.25
Nitrobenzene	33.9	Acetic Acid	4.79
Benzene	12.0	Ethyl Acetate	12.6
Cyclohexane	1.51		

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 equation (6), a biparametric equation involving π^* and β, and separately with π^* and β are given below as equations (7) - (10).

$$\log k_2 = -3.71 + 1.34 \,(\pm 0.15)\, \pi^* + 0.18 \,(\pm 0.13)\, \beta + 0.23 \,(\pm 0.12)\, \alpha \tag{7}$$

$R^2 = 0.8850$, $sd = 0.14$, $n = 18$, $\psi = 0.37$

$$\log k_2 = -3.76 + 1.43 \,(\pm 0.16)\, \pi^* + 0.10 \,(\pm 0.13)\, \beta \tag{8}$$

$R^2 = 0.8560$, $sd = 0.15$, $n = 18$, $\psi = 0.40$

$$\log k_2 = -3.74 + 1.45 \,(\pm 0.15)\, \pi^* \tag{9}$$

$r^2 = 0.8502$, $sd = 0.26$, $n = 18$, $\psi = 0.40$

$$\log k_2 = -2.93 + 0.36 \,(\pm 0.31)\, \beta \tag{10}$$

$r^2 = 0.0761$, sd = 0.37, $n = 18$, $\psi = 0.99$

Here n is the number of data points and ψ is the Exner's statistical parameter[13].

Kamlet's[12] triparametric equation explains *ca.* 89% of the effect of solvent on the oxidation. However, by Exner's criterion[13] the correlation is not even satisfactory (*cf.* Eqn. 7). The major contribution is of solvent polarity. It alone accounted for *ca.* 85 % of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's[14] equation (10) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \tag{11}$$

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 equation (11), separately with A and B and with ($A + B$).

$$\log k_2 = 0.37 + (\pm 0.04)\, A + 1.47 \,(\pm 0.03)\, B - 3.88 \tag{12}$$

$R^2 = 0.9939$, $sd = 0.03$, $n = 19$, $\psi = 0.08$

$$\log k_2 = 0.16\ (\pm 0.48)\ A - 3.87 \qquad (13)$$

$$r^2 = 0.0068,\ sd = 0.39,\ n = 19,\ \psi = 1.02$$

$$\log k_2 = 1.44\ (\pm 0.07)\ B - 3.76 \qquad (14)$$

$$r^2 = 0.9595,\ sd = 0.08,\ n = 19,\ \psi = 0.24$$

$$\log k_2 = 1.11 \pm 0.14\ (A + B) - 3.84 \qquad (15)$$

$$r^2 = 0.7813,\ sd = 0.18,\ n = 19,\ \psi = 0.48$$

The rates of oxidation of TLA in different solvents showed an excellent correlation in Swain's equation (cf. Eqn. 12) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 96% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by $(A + B)$, also accounted for *ca.* 78% of the data. In view of the fact that solvent polarity is able to account for *ca.* 78% 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 ($r^2 = 0.5151,\ sd = 0.27,\ \psi = 0.71$).

Mechanism

The lack of any effect of radical scavenger, such as acrylonitrile on the reaction rate and the failure to induce the polymerisation of acrylonitrile, point against the operation of a one-electron oxidation giving-rise to free radicals. The observed solvent effect supports a transition state, which is more polar than the reactant state. The observed Michaelis-Menten type of kinetics with respect to thioacids also leads us to suggest the formation of thioester as an intermediate. It is therefore, proposed that the reaction involves the formation of an ester intermediate and its subsequent decomposition in the slow step (Scheme 1).
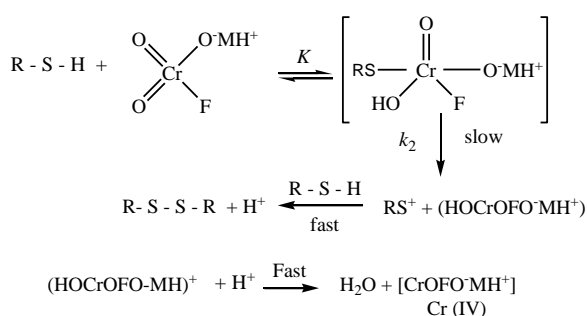
Scheme 1. Mechanism of oxidation of thioacids by MFC.

The formation of a sulphenium cation, in the rate-determining step, is also supported by the observed major role of cation-solvating power of the solvents.

It is of interest to compare here the reaction patterns of the oxidation of thioacids by other halochromates (QFC,[15] QBC[16] and MCC[17]) and MFC.

QFC and MFC represented a Michaelis-Menten type of kinetics with respect to thioacid, whereas the oxidation by QBC and MCC exhibited a second order kinetics, first with respect to each reactant. This may be due to a very low value of the formation constant of the thioester. The solvent effect and [H^+] ion dependence are parallel in all the reactions.

Acknowledgements

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