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Kinetics and Mechanism of Oxidation of some Thioacids by Pyridinium Dichromate

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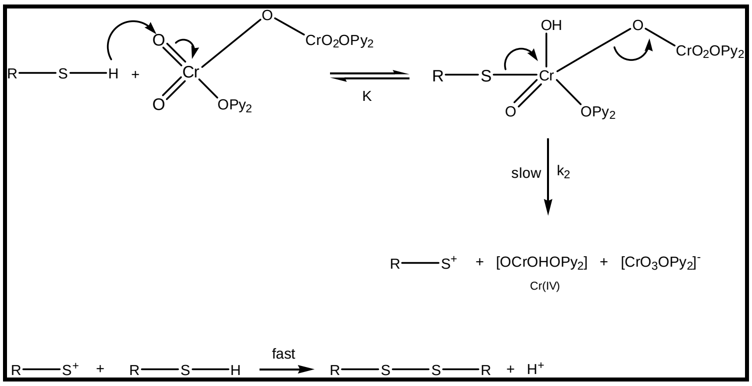
ABSTRACT

Oxidation of thioglycolic, thiolactic and thiomalic acids by pyridinium dichromate (PDC) in dimethylsulphoxide (DMSO) leads to the formation of disulphide dimmers. The reaction is first order in PDC. Michaelis-Menten type of kinetics is observed with respect to the thioacids. Reaction is failed to induce the polymerisation of acrylonitrile. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has taking 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.*

Graphical Abstract



Scheme

Keywords: Dichromate, Kinetics, Mechanism, Oxidation, Thioacids.

INTRODUCTION

Most of the salts of Cr (VI) which have already been used in synthetic organic chemistry are drastic and non-selective in nature. It has been noticed that these reagents are insoluble in most of the organic solvents. To overcome these restrictions various derivatives of Cr (VI) derivatives were introduced in synthetic organic chemistry as mild and selective oxidizing reagents in non-aqueous solvents [1]. Pyridinium dichromate (PDC) is also one of the compounds used for the purpose [2]. Only a few reports are available in the literature regarding its oxidation aspects [3-6]. We report in the present article the kinetics of oxidation of thioglycolic acid (TGA), thiolactic acid (TLA) and thiomalic acids (TMA) by PDC in dimethylsulphoxide (DMSO) as solvent. Some mechanistic aspects are also discussed.

MATERIALS AND METHODS

Materials: The thioacids (Fluka) and dithiodiglycollic acid (Sigma 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 [7]. 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 [7, 8]. PDC was prepared by the reported method [2] and its purity was checked by an iodometric method. The solvents were purified by usual methods [9]. p-toluene sulphonic acid (TsOH) was used as a source of hydrogen ions.

Stoichiometry: Stoichiometric determinations, as well as the characterization of the products, carried out polarographically [10, 11] using an automatic (Heyrovsky TP 55A). It was found that the cathode wave given by a known sample of disulphide dimmer 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 PDC reduced. Further, the reaction mixtures with an excess of PDC were allowed to go to completion and the residual PDC was determined iodometrically. These results also gave a 1:2 stoichiometry. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method, is 3.90±0.10.

$$2R-S-H + Cr_2O_7^{-2} + 12H^+ \longrightarrow R-S-S-R + 7H_2O + 2Cr^{+3} \qquad (1)$$

Kinetic measurements: The reactions were carried out under pseudo-first-order conditions by keeping a large excess (× 15 or greater) of the thioacids over PDC. 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 [PDC] at 361 nm on a spectrophotometer (AIMIL, India, Model MK-II). The PDC showed a λ_{max} of 361 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 [PDC] against time. Duplicate kinetic runs showed that the rate constants are reproducible to within ±3%. The second order rate constants were evaluated from the relation $k_2 = k_{obs}/[\text{reductant}]$. All reactions, other than those to study the effect of $[H^+]$, were performed in the absence of TsOH.

RESULTS AND DISCUSSION

Kinetics dependence: The reactions are of first order with respect to PDC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of PDC. The reaction rate increases with increase in the concentration of the thioacid but not linearly (Table 1). Figure 1 depicts a typical kinetic run. A plot of $1/k_{obs}$ against 1/[Thioacid] is linear ($r > 0.995$) with an intercept on the rate-ordinate (Figure 2). 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).

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

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

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

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

10^3 [PDC] (mol dm^{-3})	[Thioacid] (mol dm^{-3})	10^4 k_{obs} (s^{-1})		
		TGA	TLA	TMA
1.0	0.10	3.99	12.2	5.36
1.0	0.20	6.16	18.0	8.06
1.0	0.40	8.46	23.6	10.8
1.0	0.60	9.66	26.3	12.1
1.0	0.80	10.4	27.9	12.9
1.0	1.00	10.9	29.0	13.5
1.0	1.50	11.6	30.5	14.3
1.0	3.00	12.5	32.3	15.2
2.0	0.40	8.82	24.3	11.7
4.0	0.40	8.10	23.4	9.99
6.0	0.40	8.37	24.9	10.5
8.0	0.40	8.01	22.5	9.81
1.0	0.20	6.39*	19.8*	8.28*

* contained 0.001 M acrylonitrile

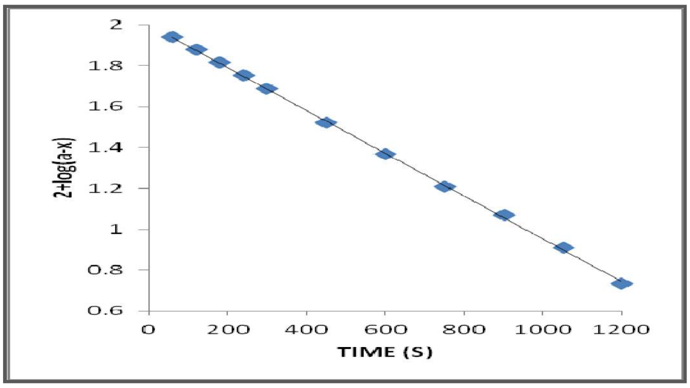


Figure 1. Oxidation of thioglycolic acid by PDC: A typical kinetic run.

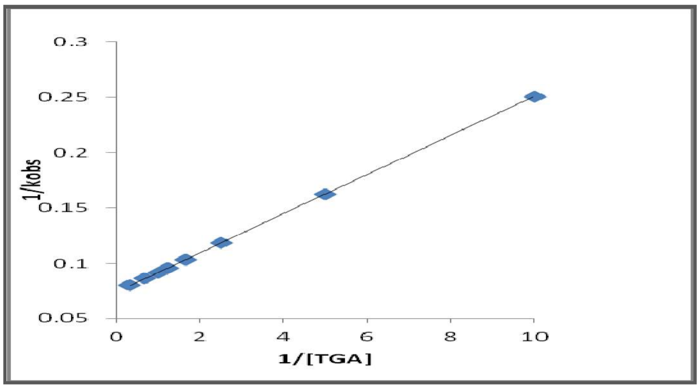


Figure 2. Oxidation of thioglycolic acid by PDC: A double reciprocal plot.

Table 2. Effect of Hydrogen ion Concentration on the Oxidation of thioacids by PDC

[PDC] = 0.001 mol dm^{-3};		**[Thioacids] = 1.0 mol dm^{-3};**				**Temp. = 298 K**
[H$^+$]/mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00
TGA	4.68	5.76	6.66	7.74	10.1	10.8
TLA	14.4	16.2	21.6	23.4	30.6	34.2
TMA	6.30	7.20	9.18	10.8	13.5	15.3

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 3 and 4).

Table 3. Rate constants for the decomposition of PDC–Thioacids complexes and their activation parameters

Thioacid	**$10^3 k_2$ / (dm^{-3} mol^{-1} s^{-1})**				**ΔH^***	**$-\Delta S^*$**	**ΔG^***
	288 K	**298 K**	**308 K**	**318 K**	**(kJ mol^{-1})**	**(J mol^{-1}K^{-1})**	**(kJ mol^{-1})**
TGA	6.93	13.5	24.3	44.1	44.2±0.3	133±1	83.7±0.3
TLA	34.2	58.5	99.9	162	37.1±0.2	145±1	80.0±0.2
TMA	16.2	28.8	53.1	89.1	41.1±0.5	137±2	81.7±0.4

Table 4. Formation constants for the decomposition of PDC–Thioacids complexes and their thermodynamic parameters

Thioacid	**K / (dm^3 mol^{-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	5.04	4.20	3.48	2.68	18.3±0.9	42±3	6.01±0.7
TLA	5.58	4.80	3.93	3.15	17.0±0.8	36±2	6.31±0.6
TMA	4.95	4.18	3.33	2.55	19.3±1.0	45±3	5.95±0.8

Induced polymerization of acrylonitrile: The oxidation of thioacids by PDC, 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.

Effect of acidity: The reaction is catalysed by hydrogen ions (Table 3). The hydrogen- ion dependence has the following form $k_{obs} = a + b\,[H^+]$. The values of a and b, for TLA, are $11.9 \pm 0.87 \times 10^{-3}$ s^{-1} and $22.2 \pm 1.43 \times 10^{-3}$ mol^{-1} dm^3 s^{-1} respectively ($r^2 = 0.9837$).

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 PDC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The dependence of rate on [Thioacid] and [PDC] were studied in all the solvents. The kinetics were similar in all the solvents. The values formation constants K and decomposition constants k_2 for TLA-PDC complexes at 298 K are recorded in table 4. The formation constant of the intermediate complex, K, did not vary much with the solvent but the rate constant, k_2, exhibited much variation in values with different solvents (Table 5).

Solvent effect: 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] (5).

$$\log k_2 \;=\; A_0 \;+\; p\pi^* \;+\; b\beta \;+\; a\alpha \qquad (5)$$

Table 5. Effect of solvents on the oxidation of TLA-PDC complex at 298 K

Solvents	**K (dm^{-3} mol^{-1})**	**10^3 k_{obs} (s^{-1})**	**Solvents**	**K (dm^{-3} mol^{-1})**	**10^3 k_{obs} (s^{-1})**
Chloroform	5.58	47.9	Toluene	4.69	14.8
1,2-Dichloroethane	6.01	58.9	Acetophenone	5.13	63.1
Dichloromethane	5.76	44.7	THF	5.34	27.5
DMSO	4.20	135	t-Butylalcohol	5.45	17.8
Acetone	4.48	53.7	1,4-Dioxane	6.03	30.9
DMF	5.82	69.2	1,2-Dimethoxyethane	6.11	17.0
Butanone	5.63	41.7	CS_2	5.77	8.13
Nitrobenzene	5.22	57.5	Acetic Acid	5.69	9.77
Benzene	5.91	22.4	Ethyl Acetate	5.82	19.9
Cyclohexane	5.55	2.82			

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 (5), a biparametric equation involving π^* and β, and separately with π^* and β are given below as equations (6) - (9).

$$\log k_2 = -3.55 + 1.38 (\pm 0.18)\, \pi^* + 0.13 (\pm 0.15)\, \beta + 0.17 (\pm 0.14)\, \alpha \qquad (6)$$
$$r^2 = 0.8394; \quad sd = 0.17; \quad n = 18; \quad \psi = 0.45$$

$$\log k_2 = -3.51 + 1.44 (\pm 0.18)\, \pi^* + 0.07 (\pm 0.15)\, \beta \qquad (7)$$
$$r^2 = 0.8240; \quad sd = 0.17; \quad n = 18; \quad \psi = 0.44$$

$$\log k_2 = -3.53 + 1.46 (\pm 0.17)\, \pi^* \qquad (8)$$
$$r^2 = 0.8213; \quad sd = 0.17; \quad n = 18; \quad \psi = 0.43$$

$$\log k_2 = -3.64 + 0.33 (\pm 0.32)\, \beta \qquad (9)$$
$$r^2 = 0.0618; \quad sd = 0.38; \quad n = 18; \quad \psi = 0.99$$

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

Kamlet's [12] triparametric equation explains *ca.* 84% of the effect of solvent on the oxidation. However, by Exner's criterion [13] the correlation is not even satisfactory (*cf.* equation 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 analyzed in terms of Swain's [14] equation (10) of cation- and anion-solvating concept of the solvents also.

$$\log k_2 = aA + bB + C \qquad (10)$$

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 analyzed in terms of equation (10), separately with A and B and with (A + B).

$$\log k_2 = 0.47 + (\pm 0.05)\, A + 1.51 (\pm 0.04)\, B - 4.34 \qquad (11)$$
$$r^2 = 0.9895; \quad sd = 0.04; \quad n = 19; \quad \psi = 0.11$$

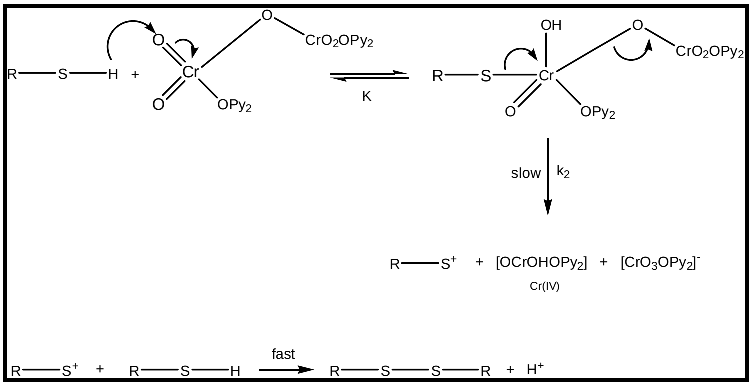
$$\log k_2 = 0.26 (\pm 0.50)\, A - 3.62 \qquad (12)$$
$$r^2 = 0.0153; \quad sd = 0.41; \quad n = 19; \quad \psi = 1.02$$

$$\log k_2 = 1.48\,(\pm 0.09)\,B - 4.49 \qquad (13)$$
$$r^2 = 0.9384;\ sd = 0.10;\ n = 19;\ \psi = 0.25$$

$$\log k_2 = 1.17 \pm 0.14\,(A + B) - 4.37 \qquad (14)$$
$$r^2 = 0.8111;\ sd = 0.18;\ n = 19;\ \psi = 0.45$$

The rates of oxidation of TLA in different solvents showed an excellent correlation in Swain's equation (cf. equation 11) with the cation-solvating power playing the major role. In fact, the cation-solvation alone account for *ca.* 94% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 81% of the data. In view of the fact that solvent polarity is able to account for *ca.* 81% 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 ($r^2 = 0.5319$; sd = 0.27; $\psi = 0.72$).

Mechanism: The lack of any effect of radical scavenger, such as acrylonitrile on the reaction rate and the failure to induce the polymerization 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. (Scheme1)



Scheme 1

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 like (QFC [15], QBC [16] MCC [17] and dichromates like TPSD [18] and with PDC. QFC and PDC 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 is parallel in all the reactions.

APPLICATION

It is widely believed that an understanding of a chemical reaction can be achieved only through investigation of the mechanism by which the changes occur. It is applied to almost all types of reactions.

CONCLUSION

Oxidation of thioacids involves the formation of a thioester and its decomposition in the rate-determining step, further it is also supported by the cation-solvating power of the solvents.

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