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ORIGINAL ARTICLE

Oxidation of 3,4,5-trimethoxybenzaldehyde by pyridinium fluorochromate in N,N-dimethyl formamide medium: A kinetic and mechanistic study

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N,N-Dimethyl formamide

Abstract Kinetics of oxidation of 3,4,5-trimethoxybenzaldehyde (TMBA) by pyridinium fluorochromate (PFC) in N,N-dimethyl formamide (DMF) medium in the presence of toluene *para*-sulfonic acid (TsOH) has been studied. The reaction is first order each in [PFC], [TMBA] and [TsOH]. The rate of oxidation remains unaltered by the variation of $NaClO_4$ but addition of $MnSO_4$ decreases the rate. The effects of the dielectric constant of the medium and the ionic strength indicate the reaction to be of ion–dipole type. The stoichiometry of the reaction is 1:1 and the product of oxidation is the corresponding 3,4,5-trimethoxybenzoic acid and Cr(III). The reaction rates have been determined at different temperatures and the activation parameters were calculated. The reaction failed to induce the polymerization of acrylonitrile, i.e., absence of free radicals. A suitable mechanism involving the slow formation of an unstable chromate ester and a rate law has been proposed.

1. Introduction

Aromatic and aliphatic aldehydes have many applications. Aromatic aldehydes act as a key chemical intermediate for the production of a variety of fine or special chemicals, such as pharmaceuticals, drugs, dyestuffs, pesticides and perfume composition. 3,4,5-Trimethoxybenzaldehyde is used as an intermediate for the synthesis of various pharmaceuticals especially for trimethoprim used to treat various bacterial infections, esp. urinary tract pathogens in combination with sulfamethoxazole (Roth and Kleemann, 1988). So it is very important to know the mechanistic aspects of oxidation of such aldehydes.

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occur-

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Abbreviations: TMBA, 3,4,5-trimethoxybenzaldehyde; PFC, pyridinium fluorochromate; DMF, N,N-dimethyl formamide; TsOH, toluene *para*-sulfonic acid.

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ring organic compounds, and has a wide range of applications spanning the synthesis of sulfur nanoparticles and the determination of biological oxygen demand in organic polluted water (Lan et al., 2005). Cr(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic (Losi et al., 1994; Viamajala et al., 2004), so there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates.

A variety of compounds containing chromium(VI) like butyltriphenylphosphonium dichromate (Dilsha and Kothari, 2009), morpholinium chlorochromate (Soni et al., 2008), isoquinolinium bromochromate (Khansolea et al., 2009), pyridinium chlorochromate (Hiran et al., 2009, 2010), pyridinium bromochromate (Hiran et al., 2002, 2004; Vanangamudi and Srinivasan, 2009), quinolinium bromochromate (Hiran et al., 2007), imidazolium fluorochromate (Thirumoorthy et al., 2010), and benzyltriphenylphosphonium chlorochromate (Ghammamy et al., 2009) have been proved to be versatile reagents capable of oxidizing almost every oxidizable functional group (Wiberg, 1965). One such compound is pyridinium fluorochromate; a stable bright orange crystalline compound found to be a mild selective reagent for the oxidation of organic substrates.

Oxidation of aldehydes into the corresponding carboxylic acids is one of the important methods in organic synthesis as the carboxylic acids are versatile intermediates in a variety of synthetic transformations (Sheldon and Bekkum, 2001). A number of aromatic aldehydes have been oxidized by oxidants like imidazolinium dichromate (Mansoor and Shafi, 2009), quinolinium dichromate (Bowden et al., 1964), quinolinium bromochromate (Hiran et al., 2007; Nalwaya, 2002), pyridinium bromochromate (Joshi, 2002), quinolinium fluorochromate (Pandurangan and Murugesan, 1995), 4(dimethylamino) pyridinium chlorochromate (Krishnasamy et al., 2007), in aqueous media.

Literature survey has also unveiled the fact that the study of oxidation of aromatic aldehyde like TMBA in non-aqueous medium is lacking. Hence the present investigation is an effort to probe into the kinetic and mechanistic aspects of PFC oxidation of TMBA in DMF.

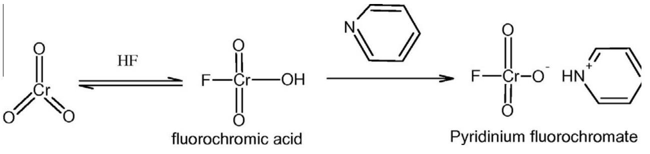
2. Experimental

2.1. Materials and methods

Analytical reagent grade chemicals of high purity were used. Doubly distilled AnalaR grade DMF (Thomas Baker Ltd.) was used as a source of solvent.

2.2. Preparation of the oxidant (pyridinium fluorochromate)

PFC was prepared in the lab by the method described by Bhattacharjee et al. (1982), and its purity was checked by iodometric method, m.p. determination and IR spectral analysis [υ_{max}(KBr) = 3033, 2366, 1616, 1466, 1299, 949, 733 cm^{-1}]. The m.p. of PFC was obtained at 413 K which was confirmed with the literature value (413–415 K). The stock solution of PFC was prepared in DMF and it was stable. λ_{max} was observed at 354 nm.



3,4,5-Trimethoxybenzaldehyde (white crystalline powder with light yellow color, A.R. grade, S.d. Fine-chem. Ltd.) was a commercial product used as such. It is slightly soluble in water, soluble in DMF, ethanol, acetic acid, ethyl ether chloroform, etc. Its purity was checked by m.p. and by TLC (4:1 ether–hexane) which revealed only one spot and R_f value comes out to be 0.57 (Slotta and Heller, 1930). Stock solution of TMBA was prepared by direct dissolving of a known volume in DMF medium. It was stored in refrigerator and used up to 1 week.

2.3. Standardization of 3,4,5-trimethoxybenzaldehyde

The solution of TMBA was standardized by the following method. In a 250 mL conical flask, 2 mg of 3,4,5-trimethoxybenzaldehyde was taken and dissolved in DMF medium. To this, 50 mL of 0.1 N sodium bisulfate solution prepared in DMF was added and was shaken vigorously. It was allowed to stand for half an hour. The excess bisulfate was titrated against 0.1 N iodine solution using starch as an indicator. A blank titration taking 50 mL of sodium bisulfate solution was also performed in a similar method and the quantity of TMBA was estimated by the difference in the volumes of iodine (I_2) used (U.S. Department of Health Education and Welfare, 1973):

$$50\ \text{mL of NaHSO}_3 = V\ \text{mL of I}_2$$

$$\text{Excess of NaHSO}_3 = V_1\ \text{mL of I}_2$$

$$V - V_1\ \text{mL of I}_2 = [\text{aldehyde}]$$

$$> C{=}O + NaHSO_3 \rightarrow > C(OH)SO_3Na$$

Sodium salt of alpha-hydroxy sulfonic acid

Acetic acid (S.d. Fine-chem. Ltd., AnalaR grade) used for the solvent variation was purified by refluxing with chromium trioxide followed by distillation over $KMnO_4$. Middle fraction boiling at 390–391 K (literature value 391.5 K) was used (Dippy et al., 1959). Due to the non-aqueous nature of the solvent DMF, TsOH (S.d. Fine-chem. Ltd., AnalaR grade) was used as a source of hydrogen ion. Its purity was checked by m.p. (379 K) (Merck Index) and the stock solution of TsOH was made by direct weighing of a known amount and dissolving it in DMF. Sodium perchlorate (B.D.H., AnalaR grade) was used for determining the ionic strength. Its purity was checked by the m.p. determination. Solution of PFC in DMF obeys Beer–Lambert's Law in the concentration range of kinetic studies.

2.4. Kinetic measurements

The progress of the reaction was followed by measuring the absorbance of PFC at λ_{max} 354 nm in one cm thick cell placed in the thermostated compartment of Jasco model 7800 UV/VIS spectrophotometer (Shimadzu). No other reactant or product has any significant absorption at this wavelength. Pseudo-first order conditions were attained by keeping a large excess (×10 or greater) of the substrate over the oxidant. The reactions were carried out at a constant temperature (±0.1 K). The solvent was DMF and the reactions were followed by monitoring the decrease in the concentration of PFC up to 80% completion of the reaction. The pseudo-first-order rate constant, (k_{obs}) was evaluated from the linear

($R^2 > 0.994$) plot of log[PFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 3%. The specific rate constant, k_s, was evaluated from the relation: $k_s = k_1/[\mathrm{TMBA}][\mathrm{H}^+]$. The reactions were also carried out in DMF–acetic acid mixtures to study the effect of dielectric constant on the rate of the reactions. All reactions were performed under N_2 atmosphere.

2.5. *Stoichiometry*

In this oxidation PFC undergoes a two electron change. Oxidation state of chromium was proved by magnetic susceptibility, ESR and IR studies (Bhattacharjee et al., 1997). To determine the stoichiometry, PFC (0·001 mol) and TMBA (0·0001 mol) were made up to 100 mL DMF in the presence of 0.6 mol dm^{-3} TsOH at 303 K, in different experiments. The reaction mixture was allowed to stand for 24 h to ensure the completion of the reaction. The residual PFC was determined spectrophotometrically. Several determinations with different concentrations of PFC and TMBA showed that the reaction exhibited 1:1 stoichiometry, i.e., 1 mol of PFC was consumed with 1 mol of TMBA.

2.6. *Product analysis*

The oxidation of 3,4,5-trimethoxybenzaldehyde leads to the formation of 3,4,5-trimethoxybenzoic acid. The qualitative and quantitative product analyses were carried out under kinetic conditions, i.e., with an excess of the reductant. In a typical experiment, TMBA (0.1 mol) and PFC (0.01 mol) were made up to 50 mL with DMF and the mixture was kept in the dark for 24 h to ensure completion of the reaction in the presence of 0.6 mol dm^{-3} TsOH. After the completion of the reaction under kinetic conditions, the reaction mixture was treated with solid $NaHCO_3$ and then filtered. After complete neutralization, the reaction mixture was extracted with ether to remove unreacted TMBA. Non-aqueous layer was treated with conc. HCl drop by drop till bicarbonate was neutralized. Again add ether and shake. The product in ether was washed with cold water, dried and weighed (yield 80–85%) and identified as 3,4,5-trimethoxybenzoic acid by melting point analysis (442 K and this agreed with the literature value 441–445 K), TLC (4:1 benzene–absolute alcohol) which revealed only one spot. It was further confirmed by chemical test and FT-IR spectral analysis using KBr disc ($>$C$=$O stretching, 1686 cm^{-1}; O–H stretching, 3400 cm^{-1}; Aromatic C–H stretching, 3022.5 cm^{-1}; Aromatic C$=$C stretching, 1620.2, 1519.1 and 1320.0 cm^{-1}; asymmetric and symmetric C–H vibrations of CH_3 group are 2950 and 2840 cm^{-1}) (Fig. 1).

3. Results and discussion

TMBA is oxidized by PFC in DMF medium in the presence of TsOH at 303 K maintaining pseudo-first-order conditions and the kinetic results along with conditions are given in Tables 1–4. The product analysis and stoichiometric determination suggested the following overall reaction:

$$\mathrm{Cr(V)} + 3,4,5\text{-trimethoxybenzaldehyde} \xrightarrow{\mathrm{H}^+} 3,4,5\text{-methoxybenzoic acid} + \mathrm{Cr(III)}$$

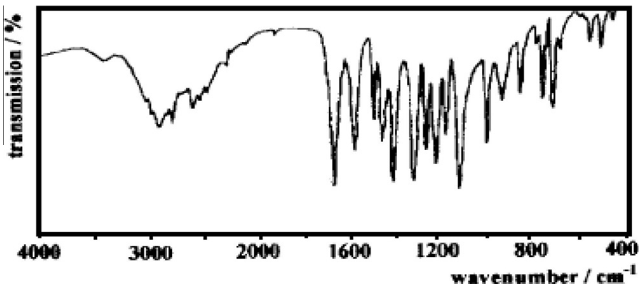


Figure 1 Spectra of 3,4,5-trimethoxybenzoic acid taken by Perkin–Elmer FTIR 1725X spectrometer.

3.1. *Stability of the oxidant (pyridinium fluorochromate)*

The solution of PFC in DMF solvent obeys Beer–Lambert's Law at λ 354 nm. There was no change in optical density and spectra of PFC solution, without substrate in DMF on long standing or heating up to 333–343 K.

3.2. *Effect of varying oxidant concentration*

The concentration of PFC was varied in the range 0.25×10^{-3}–2.50×10^{-3} mol dm^{-3} at constant [TMBA], [TsOH] at 303 K and the rates were measured. (Table 1) The near constancy in the value of k_{obs} (pseudo-first-order rate constant) irrespective of the concentration confirms the first order dependence on PFC.

3.3. *Effect of varying substrate concentration*

The concentration of the substrate TMBA was varied in the range 0.50×10^{-2}–3.00×10^{-2} mol dm^{-3} at 303 K and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The rate of oxidation increased progressively on increasing the concentration of TMBA. The plot of log k_1 *versus* log[TMBA] gave the slope of 1.112 ($R^2 = 0.99$) indicating first order dependence on TMBA. Under pseudo-first-order conditions, the plot of $1/k_1$ *versus* $1/[S]$ (where S is the substrate concentration) was linear with a negligible intercept indicating that the intermediate formed in a slow step got consumed in a subsequent fast step.

3.4. *Effect of toluene para-sulfonic acid*

TsOH has been used as a source of H^+ in reaction medium. The concentration of TsOH was varied in the range 0.20–1.60 mol dm^{-3} keeping all other reactant concentration as constant at 303 K and the rates were measured (Table 1). The acid catalyzed nature of this oxidation is confirmed by an increase in the rate on the addition of TsOH. The plot of k_1 *versus* log[H^+] is a straight line ($R^2 = 0.993$) with a slope of 1.066. Therefore, order with respect to H^+ is one. PFC may become protonated in the presence of acid. The protonated PFC may function as an effective oxidant (Bhattacharjee et al., 1984) similar to that of chromium trioxide oxidation (Wiberg, 1965). Protonated PFC is likely to be a better electrophile and a better oxidant compared to a neutral one. The effects of the dielectric constant of the medium and the ionic strength indicate the reaction to be of ion–dipole type. Thus in the

Table 1 Effect on rate by variation of [PFC], [TMBA], [PTSA] and temperature on oxidation.

[PFC] ($\times 10^3$ mol dm^{-3})	[TMBA] ($\times 10^2$ mol dm^{-3})	[PTSA] ($\times 10^1$ mol dm^{-3})	Temperature (K)	k_1 ($\times 10^4$ s^{-1})
0.25	1.00	6.0	303	15.35
0.75	1.00	6.0	303	14.97
1.00	1.00	6.0	303	15.74
1.75	1.00	6.0	303	15.74
2.50	1.00	6.0	303	15.81
1.00	**0.5**	6.0	303	7.29
1.00	**1.00**	6.0	303	15.35
1.00	**2.00**	6.0	303	36.85
1.00	**2.50**	6.0	303	43.76
1.00	**3.00**	6.0	303	51.43
1.00	1.00	**0.0**	303	1.92
1.00	1.00	**2.0**	303	5.37
1.00	1.00	**6.0**	303	15.74
1.00	1.00	**14.0**	303	35.70
1.00	1.00	**16.0**	303	42.22
1.00	1.00	6.0	**298**	12.28
1.00	1.00	6.0	**303**	15.35
1.00	1.00	6.0	**308**	19.57
1.00	1.00	6.0	**313**	26.87
1.00	1.00	6.0	**318**	39.53
1.00	1.00	6.0	**323**	54.89
1.00	1.00	6.0	303	15.74[a]

Note: The values which are in bold signifies the variation in concentration of each PFC, TMBA and PTSA along with the change in temperature and the variation are used to see the effect on the rate of reaction.

[a] Contained 0.001 mol dm^{-3} acrylonitrile.

reaction mechanism the protonated PFC species behaves as a dipole.

Table 2 Thermodynamic activation parameters.

Activation Parameters	Values
Energy of activation, $\Delta E_a^{\#}$	48.46 kJ mol^{-1}
Enthalpy of activation, $\Delta H^{\#}$	45.94 kJ mol^{-1}
Entropy of activation, $\Delta S^{\#}$	-100.31 J K^{-1} mol^{-1}
Frequency factor, pZ	5.77×10^7
Free energy change, $\Delta F^{\#}$	76.33 kJ mol^{-1}

3.5. Effect of temperature

The reactions were studied in the temperature range from 298 to 328 K to calculate the rate constants and various thermodynamic parameters (Tables 1 and 2). A plot of log k_1 *versus* $1/T$ (inverse of absolute temperature) is a straight line with negative slope. This shows that Arrhenius Equation is valid for this oxidation. The large negative value of entropy of activation $\Delta S^{\#}$ suggests slow bimolecular reaction in the rate determining step and that the rate-determining transition state is less disorderly than the reactants, i.e., a rigid transition state by an associative process (Glasstone et al., 1941). This transition state complex is unstable and the chromate ester bond breaks to form the product. According to Pearson (Basolo and Pearson, 1973) also the large negative entropy value obtained in the present study, suggests that the solvent molecules are strongly oriented or ‘frozen’ around the ions thereby resulting in the loss of entropy and accounts for the lowering of rate coefficient values with increase in the polarity of the medium.

Table 3 Effect of ionic strength on oxidation of TMBA by PFC at 303 K.

[NaClO$_4$] ($\times 10^3$ mol dm^{-3})	k_1 ($\times 10^4$ s^{-1})
0.0	15.35
1.0	15.74
3.0	15.74
5.0	15.81
7.0	14.97
8.0	15.81
9.0	15.35
10.0	15.81

3.6. Effect of ionic strength

The effect of ionic strength was studied to observe the effect of salt on the rate of oxidation in Debye–Huckel limit by varying concentration of NaClO$_4$ from 0.001 to 0.01 mol dm^{-3} provided other conditions being constant (Table 3). The rate of reaction remains almost unchanged while increasing the

Table 4 Effect of varying solvent composition on oxidation of TMBA by PFC at 303 K.

Acetic acid:DMF	Dielectric constant (D)[a]	k_1 ($\times 10^4$ s^{-1})
0:100	38.30	15.35
10:90	34.11	15.74
20:80	30.19	16.12
30:70	26.52	16.89
40:60	23.08	20.73
50:50	19.85	29.94
60:40	16.80	55.27
70:30	13.92	172.72

[a] Dielectric constant calculated by law of mixtures.

$NaClO_4$ concentration. It proves that interaction in rate determining step is not of ion–ion type (Laidler, 2005).

3.7. Effect of solvent composition

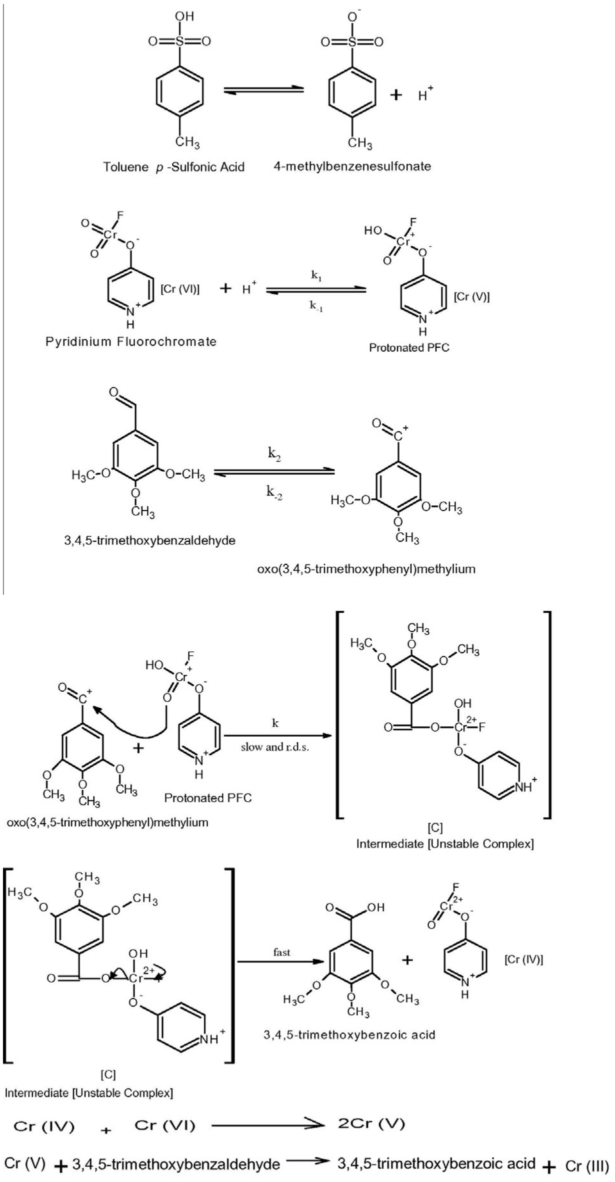
The influence of solvent polarity has been studied in acetic acid–DMF mixture. The acetic acid % (v/v) has been varied from 0% to 90% at fixed ionic strength, [TMBA], [PFC], [H^+] and temperature (Table 4). The rate of oxidation increases with decrease in polarity of solvent. In other words, a decrease in rate with increase in dielectric constant is observed, suggesting that a medium of low dielectric constant favors the oxidation process. This is due to polar character of the transition state as compared to that of reactants. The plot of $\log k_1$ *versus* $1/D$ (dielectric constant) is linear with positive slope suggesting the presence of either dipole–dipole or ion–dipole type of interaction between the oxidant and the substrate (Scatchard, 1932, 1939). Plot of $\log k_1$ *versus* $(D - 1)/(2D + 1)$ is a curvature indicating the absence of dipole–dipole interaction in the rate determining step. Positive slope of $\log k_1$ *versus* $1/D$ plot indicates that the reaction involves a cation–dipole type of interaction in the rate determining step. Amis (1967) holds the view that in an ion–dipole reaction involving a positive ionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibility of a positive ionic reactant, as the rate decreases with the increasing dielectric constant of the medium. Due to the polar nature of the solvent, transition state is stabilized, i.e., the polar solvent molecules surround the transition state and result in less disproportion.

3.8. Effect of added $MnSO_4$ concentration

In oxidation process to find out effect and involvement of various oxidation states such as [Cr(V)] and [Cr(IV)], we have studied the effect of [$MnSO_4$] on the rate of oxidation by varying in the range from 0.001 to 0.005 M (Table 5). It has been observed that addition of low concentration of Mn(II) ion can be explained by the disproportion of intermediate valence states of Cr(IV) and Cr(V). The addition of Mn(II) fixes the Cr(IV) species as Cr(III) and thus the total concentration of Cr(IV) available in a given time is lowered by the addition of Mn(II) and hence observed deceleration with increasing addition of Mn(II) ion. This may be taken as evidence for the formation of Cr(IV) species and hence PFC acts as a two-electron transfer oxidant (Chaudhary, 2002).

Table 5 Effect of [$MnSO_4$] on oxidation of TMBA by PFC at 303 K.

[$MnSO_4$] ($\times 10^3$ mol dm^{-3})	k_1 ($\times 10^4$ s^{-1})
0.0	15.74
1.0	14.58
2.0	13.82
3.0	13.05
4.0	12.28
5.0	11.51



Scheme 1

3.9. Induced polymerization of acrylonitrile

The reaction mixture in kinetic conditions to which a known amount of acrylonitrile (free from stabilizer) scavenger had been added initially, was kept for 24 h in an inert atmosphere of N_2 fails to induce the polymerization of acrylonitrile. Then on dilution of the reaction mixture with methanol, no turbidity occurred, indicating the absence of free radical intervention.

4. Mechanism and rate law

The order with respect to both [PFC] and [TMBA] is unity at fixed [H^+]. The oxidant undergoes protonation. The observed salt and solvent effects showed that the reaction is between an ion and a dipole in the slow rds and the cationic species is carbonium ion. The protonated PFC reacts with this oxo (3,4,5-trimethoxyphenyl) methylium ion (carbonium ion) to form a chromate ester which is an unstable species. This unstable complex breaks fast to form the product. Scheme 1 and rate law is proposed to explain the kinetic observations.

4.1. Rate law

$$\text{Rate} = -\mathrm{d}[\text{PFC}]/\mathrm{d}t = k[C]$$

$$R = k[\text{TMBA}^+][\text{H}^+\text{PFC}] \tag{1}$$

$$\mathrm{d}[\text{H}^+\text{PFC}]/\mathrm{d}t = k_1[\text{PFC}][\text{H}^+] - k_{-1}[\text{H}^+\text{PFC}] = 0$$

$$k_1[\text{PFC}][\text{H}^+] = k_{-1}[\text{H}^+\text{PFC}]$$

$$[\text{H}^+\text{PFC}] = k_1[\text{PFC}][\text{H}^+]/k_{-1} \tag{2}$$

$$\mathrm{d}[\text{TMBA}^+]/\mathrm{d}t = k_2[\text{TMBA}] - k_{-2}[\text{TMBA}^+] = 0$$

$$k_2[\text{TMBA}] = k_{-2}[\text{TMBA}^+]$$

$$[\text{TMBA}^+] = k_2[\text{TMBA}]/k_{-2} \tag{3}$$

Putting values of $[\text{TMBA}^+]$ $[\text{H}^+\text{PFC}]$ in (1)

$$R = kk_2/k_{-2}[\text{TMBA}]k_1/k_{-1}[\text{PFC}][\text{H}^+]$$

$$R = k_{\text{obs}}[\text{PFC}] = k_1[\text{PFC}]$$

where $k_{\text{obs}} = kk_2/k_{-2}[\text{TMBA}]k_1/k_{-1}[\text{H}^+] = k_1$.

$$k_1 = k_s[\text{TMBA}][\text{H}^+]$$

where $k_s = kk_2/k_{-2}k_1/k_{-1}$, i.e., specific rate constant

$$k_s = k_1/[\text{TMBA}][\text{H}^+]$$

This rate law is consistent with all the observed experimental results.

5. Conclusion

The oxidation of TMBA in non-aqueous medium by PFC proceeds via the formation of an unstable chromate ester which is formed in the rate determining step. This unstable chromate ester breaks to form the corresponding 3,4,5-trimethoxybenzoic acid and Cr(III). PFC acts as two electron oxidant without involvement of free radicals in this oxidation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.arabjc.2011.05.017.

References

Amis, E.S., 1967. Solvent Effects on Reaction Rates and Mechanisms. Academic Press, New York, p. 42.

Basolo, F., Pearson, R.G., 1973. Mechanism of Inorganic Reactions, A Study of Metal Complexes in Solution, second ed. Wiley-Eastern, New Delhi, p. 129.

Bhattacharjee, M.N., Choudhary, M.K., Dasgupta, H.S., Roy, N., Khathing, D.T., 1982. Pyridinium fluorochromate. Synthesis, 588–590.

Bhattacharjee, M.N., Chaudhary, M.K., Dasgupta, H.S., 1984. Bull. Chem. Soc. Jpn. 57 (1), 258–260.

Bhattacharjee, M.N., Chaudhary, M.K., Purkesyatha, S., 1997. J. Fluor. Chem. 81 (2), 211–213.

Bowden, K., Chapman, N.B., Shorter, J., 1964. J. Chem. Soc., 3370.

Chaudhary, J., 2002. Ph.D. Thesis, Mohan Lal Sukhadia University, Udaipur, Rajasthan, India.

Dilsha, K.M., Kothari, S., 2009. J. Chem. Sci. 121 (2), 189–197.

Dippy, J.F.J., Hughes, S.R.C., Rozanski, A., 1959. J. Chem. Soc., 2492.

Ghammamy, S., Baghy, M.R., Mirrahimi, M., Vaira, M.D., Javanshir, Z., Mehrani, K., Maleki, S., 2009. Trans. Met. Chem. 34, 565–570.

Glasstone, S., Laidler, K.J., Erying, H., 1941. The Theory of Rate Process. McGraw-Hill, New York (Chapters III and IV).

Hiran, B.L., Nalwaya, N., Jain, A., 2002. J. Indian Chem. Soc. 79 (1), 587–589.

Hiran, B.L., Joshi, V., Chaudhary, J., Shorgar, N., Verma, P., 2004. Int. J. Chem. Sci. 2 (2), 164–170.

Hiran, B.L., Malkani, R.K., Choudhary, P., Verma, P., Shorgar, N., 2007. Asian J. Chem. 18 (4), 3081–3086.

Hiran, B.L., Jain, S., Bhatt, C.V., 2009. E J. Chem. 6 (1).

Hiran, B.L., Meena, Munna Lal, Khuntwal, Jyoti, 2010. Der Pharma Chem. 2 (5), 470–478.

Joshi, V., 2002. Ph.D. Thesis, Mohan Lal Sukhadia University, Udaipur, Rajasthan, India.

Khansolea, S.V., Patwaria, S.B., Vibhute, A.Y., Vibhute, Y.B., 2009. Chin. Chem. Lett. 20 (3), 256–260.

Krishnasamy, K., Devanathan, D., Dharmaraja, J., 2007. Trans. Met. Chem., 922–926.

Laidler, K.J., 2005. Chemical Kinetics, third ed. Pearson Education, New Delhi, p. 198.

Lan, Y., Deng, B., Kim, C., Thornton, E.C., Xu, H., 2005. Environ. Health Sci. Technol. 39, 2087–2094.

Losi, M.E., Amrhein, C., Frankenberger, W.T., 1994. Rev. Environ. Contam. Toxicol. 136, 91–121.

Mansoor, S.S., Shafi, S.S., 2009. E J. Chem. 6 (S1), S522–S528.

Merck Index, 11th ed., p. 9459.

Nalwaya, N., 2002. Ph.D. Thesis, Mohan Lal Sukhadia University, Udaipur, Rajasthan, India.

Pandurangan, A., Murugesan, V., 1995. React. Kinet. Catal. Lett. 54 (1), 173–180.

Roth, H.J., Kleemann, A., 1988. In: Pharmaceutical Chemistry, vol. 1. Ellis Horwood, Chichester, UK, p. 286.

Scatchard, G.J., 1932. Chem. Phys. 10, 229.

Scatchard, G.J., 1939. Chem. Phys. 7, 657.

Sheldon, R.A., Bekkum, H.V., 2001. Fine Chemicals through Heterogeneous Catalysts, New York.

Slotta, K.H., Heller, H., 1930. Ber. Dtsch. Chem. Ges. 63, 3042.

Soni, N., Tiwari, V., Sharma, V., 2008. Ind. J. Chem. 47 (A), 669–676.

Thirumoorthy, A., Bhuvaneshwari, D.S., Elango, K.P., 2010. Int. J. Chem. Kinet. 42 (3), 159–167.

U.S. Department of Health Education and Welfare, Public Health Service, National Institute of Occupational Safety and Health, 1973. Manual of Analytical Methods, vol. 1, second ed. U.S. Department of Health Education and Welfare, Washington, DC, pp. 1251–1259.

Vanangamudi, G., Srinivasan, S., 2009. E J. Chem. 6 (3), 920–927.

Viamajala, S., Peyton, B.M., Sani, R.K., Apel, W.A., Petersen, J.N., 2004. Biotechnol. Prog. 20, 87–95.

Wiberg, K.B., 1965. Oxidation in Organic Chemistry, Part A. Academic Press/Wiley, New York, p. 69.