Pyridinium Dichromate Oxidation of Active Methylene Compounds -A Kinetic Study

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Abstract: Pyridinium dichromate in aqueous methane carboxylic acid in presence of mineral acid, oxidizes active methylene compounds such as acetyl acetone and benzoyl acetone to the corresponding pentane-2,3,4-trione and 1-phenyl, butane-1,2,3-trione. The $\frac{-dc}{dt}$ is proportional to the concentrations of first power of Pyridinium dichromate(PDC) oxidant, and H+ ions. The reactions being nearly first to zero order in substrates, while on the contrary rection completely fails to induce polymerisation of acrylonitrile. The kinetic data evaluated can be correlated with a proposed mechanistic route, involving the intermediate formation of complex at symmetrical transition state in rate determining step, which undergoes decomposition to yield the products.

Key words: Acetyl acetone, benzoyl acetone, pyridinium dichromate, oxidation, kinetics.

1. Introduction

Hexavalent chromium compounds have been widely used as oxidants reacting with diverse kinds of organic substrates. The mechanism of oxidation varies with the nature of Cr (VI) species and the solvent[1] used. The development of newer Pyridinium dichromate reagent for the oxidation of organic substrates continues to infuse keen interest.

Over the years a large number of novel PDC analogue oxidants have been introduced especially for complex or highly sensitive substances where great selectively and effectiveness, coupled with wildness of conditions are pre-requisites for success. One such oxidant is Corey's reagent PCC,[2,3] which has now emerged as useful and versatile oxidant. Moreover, it is mild, stable, efficient and economically inexpensive[4] as well as eco-friendly.

The unique properties of PDC, makes it feasible for the effective oxidation and synthesis of various compounds,[5] while on the same note structurally similar to this oxidant analogous study of its allied reagents viz. PCC, PBC,[6] and PFC,[7] employed for oxidative degradation of alcohols[8.9] and diols[10] indifferent solvent media have been reported in literature.

Synthetic organic compounds in which the active methylene group(-CH2-) is sandwiched between two carbonylgroups[11] in acetyl acetone and benzoyl acetone exist both in keto or enol form and can undergo oxidation through both the groups, having a tendency to form complexes with electrophilic species of oxidant and as an added advantage anions of these compounds are more stabilized by charge delocalisation. There are only few reports of the mechanistic pathway of oxidation reactions of above substrates available with different oxidants.[12-14] The present article deals with the kinetic aspects of active methylene compounds (acetyl acetone and benzoyl acetone) employing PDC in aqueous acetic acid medium.

2. EXPERIMENTAL

The acetyl acetone (A.R. Grade) and benzoyl acetone (E-merck) were employed after distillation under reduced pressure and immaculateness. Pyridinium dichromate (PDC) was prepared by the method as reported in literature[15] and standardization was carried by estimating Cr(VI) iodometrically before use. The sulfuric acid and acetic acid (B.D.H.) were received and were used as such. All other solutions of various reagents of required concentrations were prepared in doubly distilled water.

Kinetic Measurements

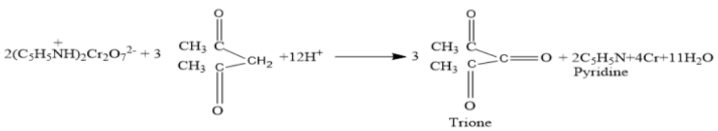
Kinetic experiments were installed in a thermostated water-bath maintained at constant temperature (±0.10C), under pseudo first-order conditions- [substrate] >> [PDC] [H+]. PDC was taken separately in a flask and reaction mixture in another flask, both were immersed in a water bath at the ambident temperature.

The thermostated solutions after attaining the bath temperature, a volume of the requisite concentration of PDC was added to the reaction contents. The reactions were performed under nitrogen atmosphere. The progress of reactions up to 75-80% completion was followed by monitoring the consumption of [PDC] iodometrically.

The reaction content was found homogenous in the solvent systems (a water- acetic acid and H+ ions). The initial rates were computed by employing integration and graphical methods and for more than two kinetic runs replicability of more than ± 3% was observed.

Stoichiometry

The stoichiometric sets were installed under atmosphere of nitrogen at 308 K. By allowing excess of [Substrate] over PDC i.e. [PDC]<< [Substrate] in aqueous acetic acid in a water bath at different acidities and the unreacted oxidant [PDC] was estimated. The stoichiometric ratios Δ [PDC] /Δ [substrate] was observed as 2/3 which confirmed to the overall an exemplary equation:



It was observed for every 3 moles of substrate, 2 moles of oxidant (PDC) are consumed. Upon addition of monomer acrylonitrile to the reaction mixture no effect on rate was observed i.e.; nullifying the existence of free radicals.
The products were characterized by measuring the m. p. and compared with the authentic samples of 2, 4-DNP derivatives of duo of triones.

3. Results and Discussions:

The pyridinium dichromate oxidative study of active methylene compounds such as acetyl acetone and benzyl acetone led to the formation of corresponding triones. No further oxidation of the product was observed under the experimental set of conditions.

The investigated reactions revealed first order rate dependency yielding straight line after plots were drawn between log [PDC] and time. The values of kobs remained almost constant on five times variation of [PDC]. The fractional order kinetics (0 < order < 1) was exhibited for active methylene compounds (acetylacetone and benzyl acetone) on five times variation of their concentrations. (Table 1).

Table. 1: Substrate dependence of the rection rate

S. No.	[Substrate] × 102 (variants) mol dm-3						
1.	Acetyl acetone (AA)	0.50	1.00	1.25	2.00	3.33	5.00
	104 k (s-1)	2.83	4.31	4.75	5.51	6.46	7.07
2.	Benzoyl acetone (BA)	1.00	1.66	2.50	3.33	4.00	5.00
	104 k (s-1)	1.92	2.52	3.26	3.81	4.07	4.42

[PDC] ×103 (mol dm-3) = 3.33 (1, 2); [H+] × (mol dm-3) = 1.66 (1, 2) ;
CH3COOH-H2O %, (v/v) = 25(1), 20 (2) ; Temp. K = 308 (1, 2)

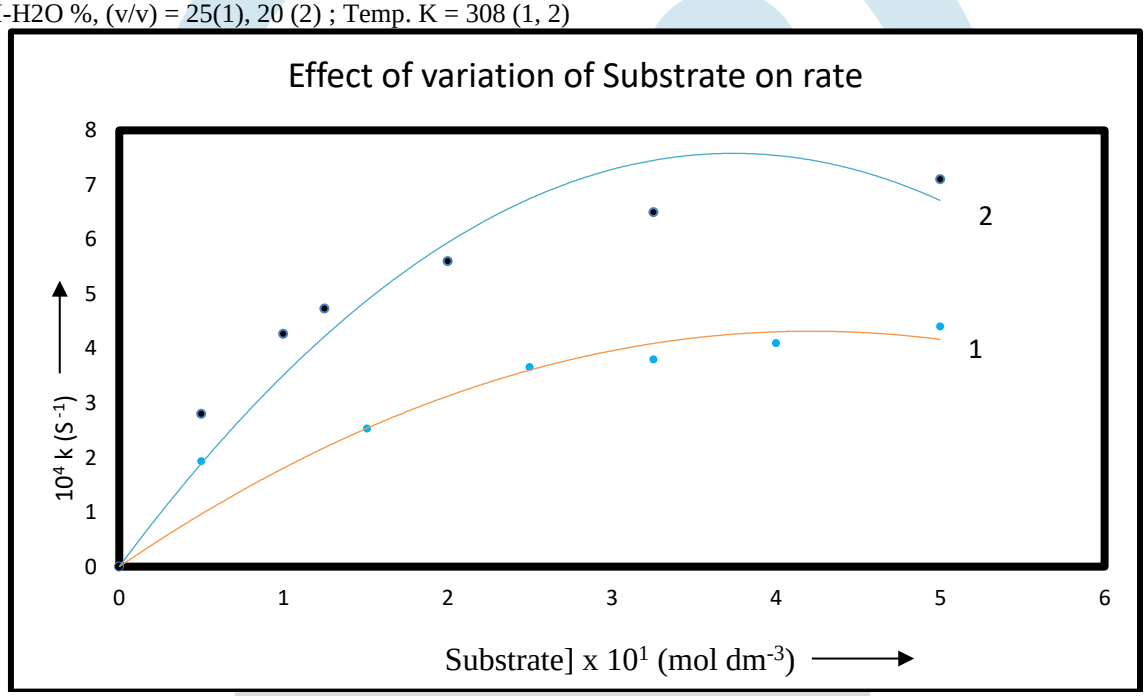


Fig.1 Plot of k vs [Substrate]
103 × [PDC] (moldm-3) =3.33 (1,2)
[H+] (mol dm-3) = 0.166 (1, 2),
CH3COOH-H2O, %, (V/V) = 25 (1), 20 (2),
Temperature, K = 308 (1, 2)
Acetyl acetone 2. benzyl acetone

The reactions followed Michaelis-Menten type kinetics which was validified by double reciprocal plot of k_{obs}^{-1}Vs. [Substrate]-1 resulting in a linear straight line with positive intercept on rate axis. (Fig. 1). The plots drawn between k(obs) and [Substrate] bends glides towards X-axis (Fig. 2) clearly indicating the presence of a complex.

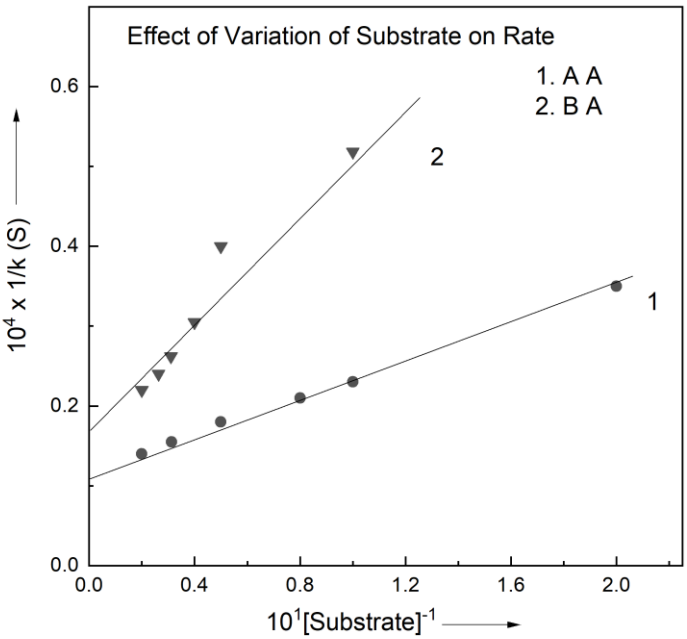


Fig.2. Double reciprocal plot of 1/k vs 1/[Substrate]
[PDC] x 10^3 (moldm^{-3}) = 3.33 (1,2);
[H^+] (mol dm^{-3}) = 0.166 (1,2);
CH_3COOH-H_2O % ,(v/v) = 25(1); 20(2),
Temperature K = 308 (1,2)

The second order constant K is variant concurring for the above view of 1-0 dependence of [Substrate].
The rates of oxidation of acetylacetone and benzyl acetone are catalysed by increase in acidity (Table. 2). The plot of log kobs vs. log [H+] is linear with positive slope, which suggests that order with respect to [H+] is one. (Fig.3)

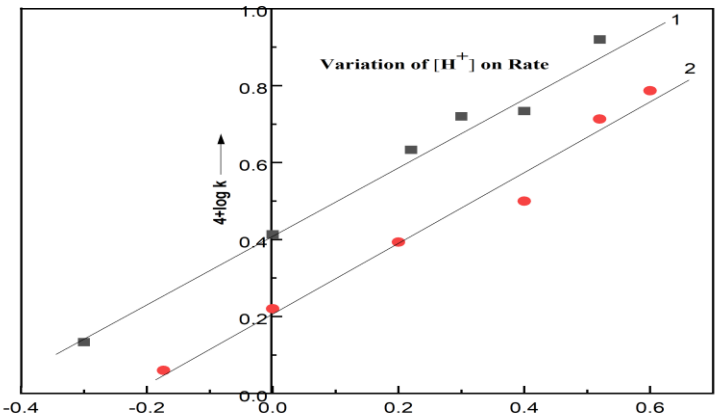


Fig.3 Plot of log k vs log [H^+]
[Substrate] x10^{-1} (mol dm^{-3}) =1.0(1),1.66 (2)
[PDC] x10^3 (mol dm^{-3}) =3.33(1-2),
[HOAc-H_2O]%(v/v) =25(1); 20 (2)
Temperature K = 308 (1-2)

Table 2: Acidity dependence of the reaction rate

[H+] (variants) mol dm-3	0.05	0.066	0.10	0.166	.20	0.25	0.333	0.40
1. Acetyl acetone (AA) 104 k (s-1)	1.36	-	2.60	4.31	5.30	6.20	8.40	-
2. Benzoyl acetone (BA) 104 k (s-1)	-	1.14	1.64	2.52	-	3.75	5.23	6.11

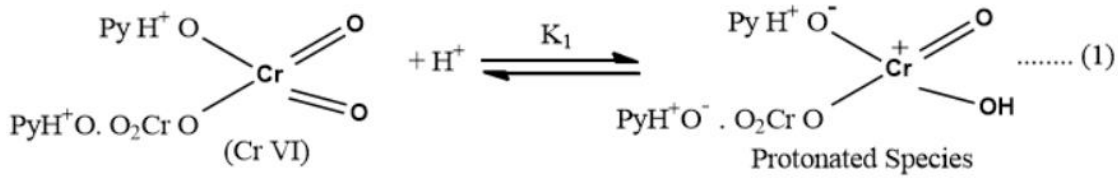
[Substrate] ×10 (mol dm-3) = 1.0 (1), 1.66 (2), [PDC] ×103 (mol dm-3) = 3.33 (1, 2),
CH3COOH-H2O %, (v/v) = 25(1), 20 (2), Temp. K = 308 (1, 2)
The variation in ionic strength (μ) i.e., addition of NaCl has had no appreciable effect on the rate of oxidation.
The oxidation of active methylene compounds by PDC was examined by varying solvent composition of acetic acid from 10% to 40 % at experimental conditions. No reaction was reported with the chosen solvents. The rate of oxidation increases markedly with

increase in proportion of CH3COOH in the medium. The Amis plots of log k Vs. 1/D were found to be linear with positive slopes a testimony towards the fact the reactions were of the ion-dipole type.

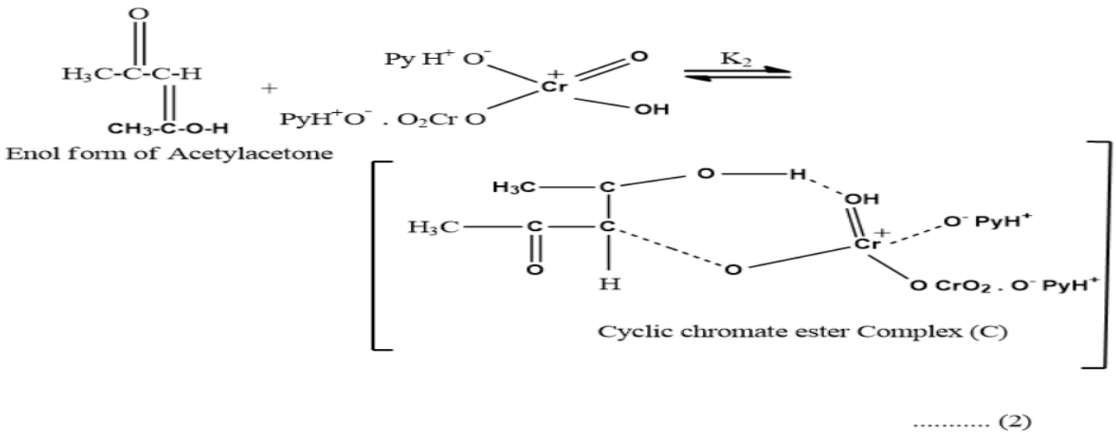
Mechanism

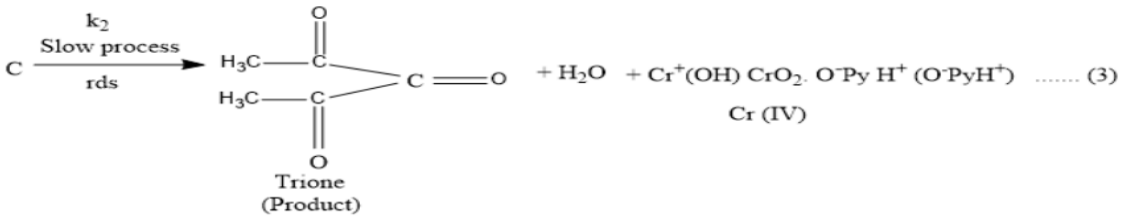
In this study, acid catalysis is accounted for substrates in terms of protonation of PDC to produce a protonated Cr (VI) species[16-20] which acts as an active electrophile/stronger oxidant [eq.1] and hence the oxidation process through PDC becomes a function of proton concentration. This fact is further evidenced by cation solvating power of the solvent. It was observed that at higher concentration of H+ ion, no levelling of rate constants occurred. The observed acid-dependence of the reaction points to a rapid reversible protonation of intermediate complex prior to its disproportionation.

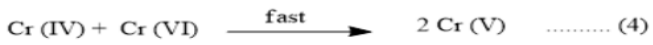
A mechanistic outline in Scheme I justifies for the experimental results.



Where Py = Pyridine (C5H5N)







Rate law

In illustrated mechanism, the rate law can be determined on applying the approximation method at steady state equilibrium condition.

$$-\frac{d}{dt}[\text{Cr (VI)} = K_2[\text{ Complex}] = k_2K_1K_2[\text{AA}]\,[\text{H}^+]\text{X}\,[\text{Cr (VI)}] \quad \ldots\ldots\ldots\ldots (1)$$

Or

$$\text{Rate} = \frac{k_2K_1\,K_2\,[\text{Cr (VI)}]_t[\text{H}^+][\text{AA}]}{1 + K_1K_2[\text{H}^+][\text{AA}]} \quad \ldots\ldots\ldots\ldots (2)$$

Since $[Cr(VI)]_t = [Cr\ (VI)] + [Complex(C)]$ ……(3)

Here [Cr (VI)]t is total concentration of Cr (vi) i.e., oxidant PDC

Where, K1 is small and produced protonated primary species which is initiates the reaction with acetyl acetone

or

$$k_{obs} = \frac{Rate}{[Cr(VI)]_t} \quad \ldots\ldots\ldots\ldots (4)$$

Substituting the values of [Cr(VI)]t in equation (2) and after simplification yields the final rate law as

$$k_{obs} = \frac{k_2K_2K_1[AA][H^+]}{1+K_1K_2[AA][H^+]} \quad \ldots\ldots\ldots\ldots (5)$$

The equation (5) well characterizes the reaction system.

Transforming the equation (5) as

$$\frac{1}{k_{obs}} = \frac{1}{k_2K_1K_2[AA][H^+]} + \frac{1}{k_2} \quad \ldots\ldots\ldots\ldots (6)$$

Reactivity

The reactivity increases in the order: Acetyl acetone > Benzyl acetone, owing to the extreme electronegative character of carbonyl moiety. The α-C-H linkage is weakened and cleaves as the electrons are displaced towards the carbon atom resulting in the loss of α-H as a proton. In these compounds the methylene group is sandwiched in between two electron attracting groups, making the molecule highly acidic, also they enolise rapidly and are stabilized by resonance due to formation of intramolecular hydrogen bonding. The slower rate of benzoyl acetone may be attributed to higher degree of enolic content (89.20 %) in compared to acetyl acetone (76.4%). In addition to this it possesses extra stability of forming chelating rings and showing conjugate effect and steric hindrance.

The replacement of methyl group of acetyl acetone by phenyl groups results in an extension of conjugated system in enol form. The proposed mechanism is also supported by the observed negative entropy of activation. The observed loss of - ΔS# justifies not only the influence of solvent but also favours postulated mechanism in the transition state too, as the two ends become extremely solvated when charge segregation occurs.

The reaction commences by oxidation of chromium metal, which reduces from Cr (VI) → Cr (IV), is believed to react with another Cr (VI) to produce Cr (V) and further it reduces to Cr (III) species in faster and terminating step. This pattern of oxidation was markedly established[21] by Cr (VI). The observed trend of reactivity indicated that the electron-releasing groups accelerate the oxidation process. The observed thermodynamic parameters, (Table 3) further validify the greater order of reactivity for acetylacetone i.e., energy of activation is lowest for acetyl acetone. It also implies that all the reactions follow an identical mechanism as values of Gibbs free energy (ΔG#) lies in the same range. The enthalpy of activation decides ultimately the fate and thermodynamic nature of reaction which is enthalpy controlled.

Table 3. Activation Parameters for the oxidation of diketones (Acetylacetone and Benzyl acetone) by Pyridinium dichromate (PDC)

Substrate	Ea kJ mol-1	ΔH# kJ mol-1	-ΔS J mol-1K-1	ΔG kJ mol-1
Acetyl acetone	48.52	46.38	120.83	83.91
Benzyl acetone	54.84	52.47	109.67	86.54

Conclusions

The oxidation of acetyl acetone and benzyl acetone by pyridinium dichromate is an acid catalysed reaction yielding the corresponding triones as the feasible product. The measured stoichiometry was found to be 3 moles of active methylene compounds consuming 2 moles of oxidant (PDC). The reactions follow Michaelis-Menten type of kinetics with respect to substrates. The protonated PDC is postulated to be the active species of oxidant reacting with the enolic form of substrate. The large negative values of ΔS# provide support for the existence and formation of rigid activated complex.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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