

# Oxidation of Active Methylene Compounds by Pyridiniumbromochromate in Acetic Acid Medium

Akanksha Shukla<sup>1\*</sup>, Vinod Dubey<sup>2</sup>

Department of Chemistry, S.G.S. Govt. P.G. College Sidhi (M.P.) India.

## Abstract

Pyridiniumbromochromate (PBC) in aqueous acetic acid oxidizes active methylene compounds to the corresponding triones. The  $-dc/dt$  is proportional to the concentrations of oxidant. The reaction is acid catalysed and the acid dependence has the form,  $k_{obs} = a + b [H^+]$ . The Michaelis-Menten type kinetics was discussed. The data can be correlated with mechanistic pathway involving the intermediate formation of chromite ester in pre-equilibrium in the transition state.

**Keywords:** acetyl acetone, benzoyl acetone, pyridiniumbromochromate, oxidation, kinetics.

## 1. INTRODUCTION

Pyridiniumbromochromate (PBC) is a heterocyclic base structurally similar to well-known Corey's reagent<sup>[1]</sup>. Pyridinium chlorochromate (PCC) and pyridinium-fluorochromate (PFC) has been successfully employed in synthetic organic chemistry. PBC a Cr(VI) derivative, is a moderate and effective has been employed as an oxidant in acid and other solvents media, such as diols<sup>[2]</sup> and alkanols by analogous oxidant PCC<sup>[3]</sup> and PFC<sup>[4]</sup>. There are only few reports in the mechanistic aspects of oxidation reactions of PBC<sup>[5-8]</sup>. Active methylene compounds viz. acetyl acetone and benzoyl acetone containing carbonyl groups<sup>[5]</sup> exhibit tautomerism. oxidized by different oxidants namely NCSA,<sup>[9]</sup> NDC,<sup>[10]</sup> IQBC,<sup>[11]</sup> PDC,<sup>[12]</sup> and QDC<sup>[13,14]</sup>, to triones. There seems to be no previous report on the oxidation mechanism of this useful reaction. The present paper deals with the oxidation of acetyl acetone and benzoyl acetone by PBC in aqueous acetic acid medium and evaluates the reaction constant ( $k_{obs}$ ).

## 2. EXPERIMENTAL

**Materials:** The synthesis and standardization of oxidant pyridiniumbromochromate (PBC) has been described earlier<sup>[15]</sup>. All employed chemical were of analR or guaranteed reagents. The solvents were purified and dried in the usual manner.<sup>[16]</sup> Double distilled water was used both for kinetics as well as reagent solution. The acetyl acetone (A.R. Grade) and benzoyl acetone (E. Merck) were used after distillation under reduced pressure. Their solutions were prepared in appropriate quantity of acetic acid.

### Kinetic procedure

The reactions were studied under pseudo first-order conditions by maintaining a large excess of the active methylene compounds over [PBC]. All the reaction mixture except PBC were taken in a separate flasks and the latter were suspended in a temperature controlled water-bath ( $\pm 0.1K$ ). The reactions were followed iodometrically. All the reactions were performed under nitrogen atmosphere.

The rate constants ( $k_{obs}$ ) were computed from the linear plots of  $\log [PBC]$  against time and were reproducible within 4%. The solvent was water and acetic acid mixture. The reaction mixture remained homogeneous in

the solvent system used.

### Product analysis

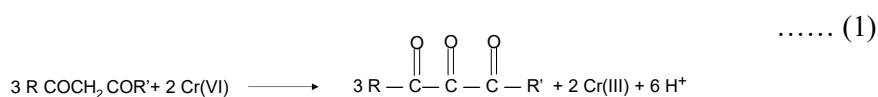
The reaction mixture was kept overnight under same experimental condition for completion of reaction. The fission product triones were characterized and estimated by the isolation of its  $75 \pm 3\%$  yields as 2,4-dinitrophenyl hydrazone.

### 3. Results and Discussion

The oxidation of the acetyl acetone and benzoyl acetone by PBC were investigated under the existing experimental conditions. There was no further oxidation of the product obtained as triones.

#### Stoichiometry

In stoichiometry determination, excess of PBC was allowed to react with substrate at various acidities and nitrogen under the condition  $[PBC]_0 > [substrate]_0$ . The unreacted [oxidant] was estimated. The overall reaction corresponds to



where, R =  $-CH_3$ , for all substrates and R =  $-CH_3$  and  $-C_6H_5$  for acetyl acetone (AA), and benzoyl acetone (BA) respectively.

The PBC mediated oxidation of substrates completely failed to induce acryloamide/acrolonitrile. The possibility of step wise electron transfer ruled out.

The order of reactions was found to be unity with respect to PBC as evidenced by the individual kinetic runs. The plot of [PBC] against time was found linear ( $r^2 = >0.997$ ). Further, the first-order rate coefficients did not vary with the initial concentrations of PBC. The order with respect to substrates was found to be of fractional-order (Table 1).

**Table 1: Dependence of rate constants on substrate concentration**

$10^3 \times [PBC]$  (mol dm<sup>-3</sup>) = 3.33 (1,2) ;  $[H^+]$  (mol dm<sup>-3</sup>) = 0.15 (1,2) ;

AcOH:H<sub>2</sub>O % (v/v) = 30 :70 (1, 2) ; Temp. K = 308 (1, 2)

$10^2$ [Diketone] mol (dm <sup>-3</sup> )	0.80	1.25	2.00	2.50	3.33	4.00	5.00	6.25
$10^4$ k (s <sup>-1</sup> ) for Acetyl acetone	2.94	4.14	5.19	-	6.09	6.38	6.61	-
Benzyl acetone	-	1.68	2.50	3.14	3.87	-	4.90	5.35

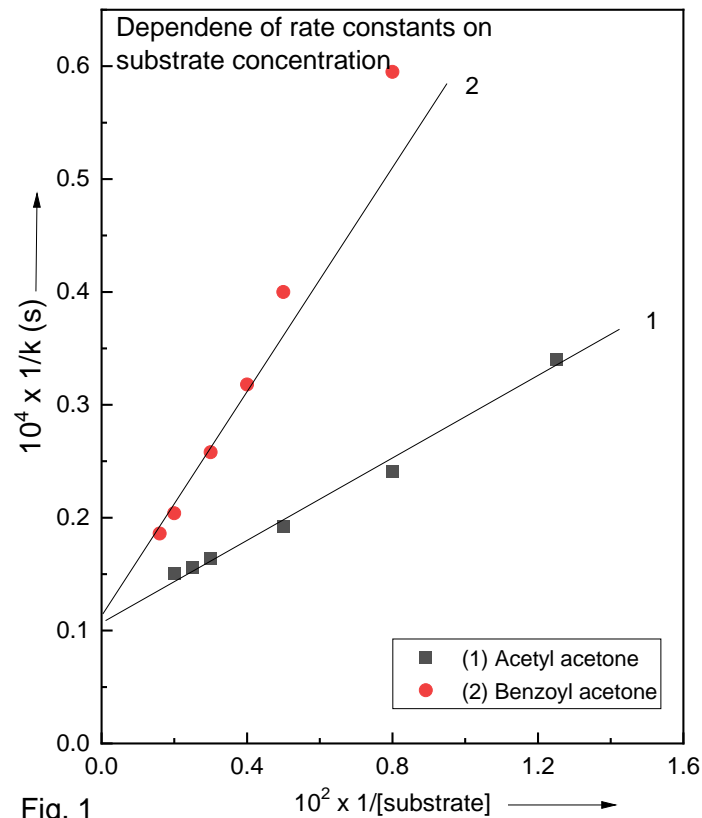


Fig. 1  
 Double reciprocal plots of  $1/k_{\text{obs}}$  vs.  $1/[\text{substrate}]$   
 $10^3 \times [\text{PBC}]$  ( $\text{mol dm}^{-3}$ ) = 3.33 (1,2) ;  
 $[\text{H}^+]$  ( $\text{mol dm}^{-3}$ ) = 0.15 (1,2) ;  
 $\text{CH}_3\text{COOH-H}_2\text{O}$  % (v/v) = 30 : 70 (1, 2) ;  
 Temp. K = 308 (1, 2)

The plot of  $\frac{1}{k_{\text{obs}}}$  vs.  $\frac{1}{[\text{diketone}]}$  yielded positive intercept on Y-axis (Fig. 1). The reaction is catalysed by acid. The catalysed reaction being nearly (0.892) first-order in acidity. The hydrogen ion dependence had the form  $k_{\text{obs}} = a + b [\text{H}^+]$ . The oxidation of substrates were studied in solution containing varying proportion of acetic acid and water (Table 2). Increasing proportion of acetic acid in the solution enhances the rate.

**Table 2: Dependence of rate constants on Solvent composition**

$10^2 \times [\text{Diketone}]$  ( $\text{mol dm}^{-3}$ ) = 1.25 (1), 2.0 (2) ;  $10^3 \times [\text{PBC}]$  ( $\text{mol dm}^{-3}$ ) = 3.33 (1, 2) ;  
 $[\text{H}^+]$  ( $\text{mol dm}^{-3}$ ) = 0.15 (1,2) ; Temp. K = 308 (1, 2)

H <sub>2</sub> O-AcOH (% , v/v)	80 : 20	70 : 30	60 : 40	50 : 50
Dielectric constant ( $10^3 \times 1/D$ )	17.17	19.15	21.98	25.64
Acetyl acetone	3.81	4.16	4.75	5.23
Benzyl acetone	2.12	2.50	2.94	3.63

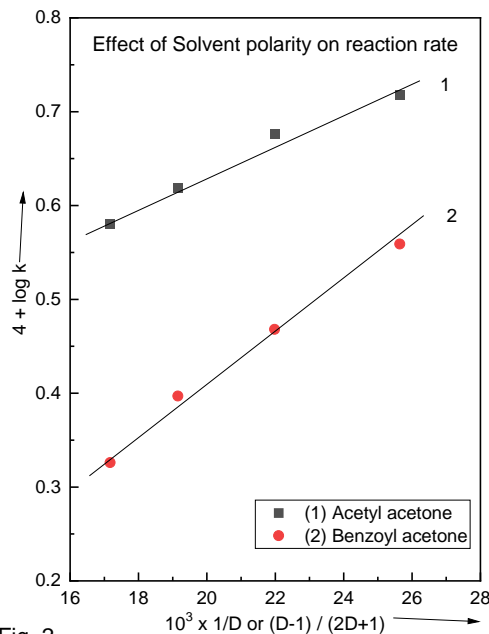


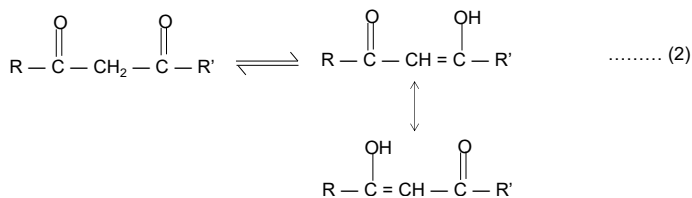
Fig. 2 Amis plot of  $\log_{10} k$  vs.  $1/D$   
 $10^2 \times [\text{Substrate}] (\text{mol dm}^{-3}) = 1.25 (1), 2.0 (2)$  ;  
 $10^3 \times [\text{PBC}] (\text{mol dm}^{-3}) = 3.33 (1, 2)$  ;  
 $[\text{H}^+] (\text{mol dm}^{-3}) = 0.15 (1,2)$  ;  
 Temp. K = 308 (1, 2)

## Discussion

The linear increase in the rate with acidity suggested the involvement of a protonated Cr(VI) species in the rate determining step. The involvement of such species are well known in chromic acid oxidation.<sup>[17]</sup> Dielectric constant can be estimated approximately from the dielectric constants of the pure solvents.<sup>[18]</sup> A plot of  $\log k$  vs. the inverse of Dielectric constant ( $D$ ) is straight line with positive slope (Fig.2). This indicates the interaction between dipole and positive ion and supports protonated Cr(VI) species in the rate-determining step. Both mineral acid and observed solvent effect support the formation of chromate ester. This intermediate is not to be very much susceptible to structural influence<sup>[19]</sup>. Hence, the observed results can be accounted as per envisaged reaction mechanism.

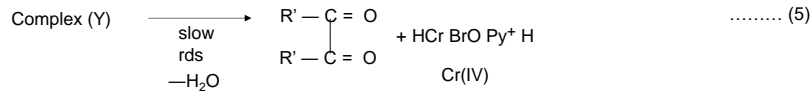
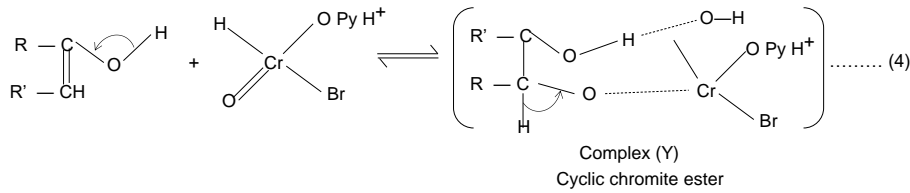
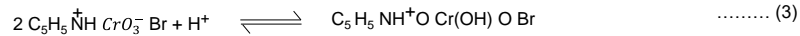
## Scheme-1

### Acid dependent paths

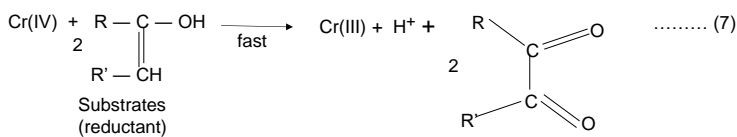
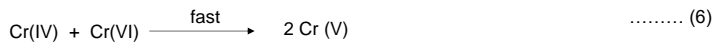


where, R and R' = -CH<sub>3</sub> for acetyl acetone (AA)

and R = -CH<sub>3</sub> and R' = -C<sub>6</sub>H<sub>5</sub> for benzoyl acetone (BA) respectively.



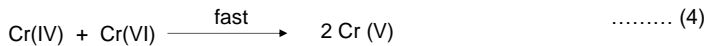
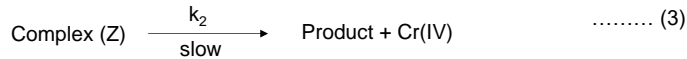
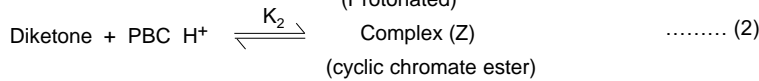
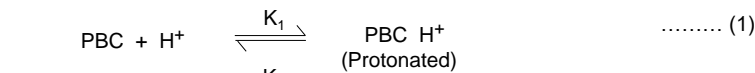
Here Cr(VI) is reduced to Cr(IV) which further reacts with another Cr(VI) to produce Cr(V)



**Integrated Rate**

Based on num

Equation may be obtained as :



The rate of reaction

$$-\frac{dc}{dt} [\text{Cr(VI)}] = k_2 [\text{Z}] \quad \dots\dots (6)$$

The final rate law leads the equation after making several calculations as :

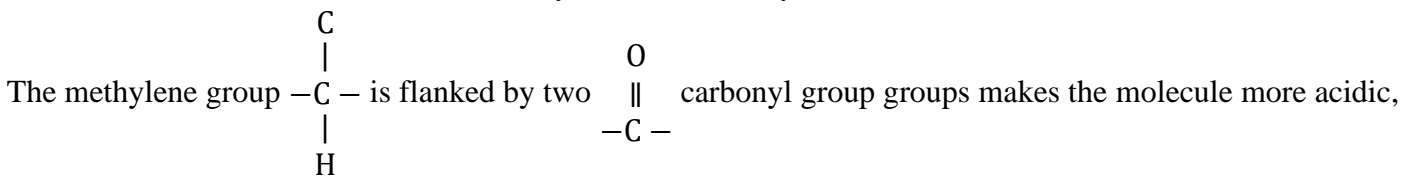
$$k_{\text{obs}} = \frac{k_2 K_1 K_2 [\text{E}][\text{H}^+]}{1 + K_1 K_2 [\text{E}][\text{H}^+]} \quad \dots\dots (7)$$

The inverse form of equation (7) gives equation (8)

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_2 K_1 K_2 [\text{E}][\text{H}^+]} + \frac{1}{k_2} \quad \dots\dots (8)$$

The above equation (8) accounts successfully all the kinetic facts of order of the reaction including Michaelis-Menten type kinetics, under investigation (1/k<sub>obs</sub> vs. 1/[diketone] with positive slope on ordinate X-axis, Fig. 1). The sequence of order of their reactivity is expressed as :

Acetyl acetone > benzyl acetone



and stabilized by resonance and intra hydrogen bonding. Despite of having higher degree of enolic content in BA, it shows slower rate than AA. It possesses capability of forming chelating ring and exhibition of steric

hinderance. The replacement of CH<sub>3</sub> group of AA by bulky phenyl group gives in an extension of conjugate system and enhance entropy. The reactivity was influenced by solvent as the two ends become extremely solvated when charge segregation occurs. The negative values of entropy of activation ( $\Delta S^\ddagger$ ) suggests a definite orientation in transition state and this is due to solvation of activated complex, the  $\Delta S^\ddagger$  is negative for both the substrates (Table 3). Hence, in conjunction with other experimental data, supports the mechanism. The energy of activation ( $E^a$ ) is lowest for the fastest reaction and vice-versa. The values of  $\Delta H^\ddagger$  are in order of activity specifically that reaction is enthalpy controlled. The near constancy of Gibbs free energy activation ( $\Delta G^\ddagger$ ) shows the same operation in all ketones and provide evidences for the above mechanistic paths in which  $\alpha$ -C-H bond is cleaved to form triones.

**Table 3: Temperature Dependence of Rate constants and Activation parameters**

$10^2 \times [\text{Diketone}] \text{ (mol dm}^{-3}\text{)} = 1.25 \text{ (1), } 2.0 \text{ (2)} ; 10^3 \times [\text{PBC}] \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (1, 2)} ;$   
 $[\text{H}^+] \text{ (mol dm}^{-3}\text{)} = 0.15 \text{ (1,2)}$

T $\pm$ 0.1 K	$\longleftrightarrow 10^4 k \text{ (s}^{-1}\text{)} \longleftrightarrow$	
	Acetyl acetone	Benzyl acetone
303	3.03	1.18
308	4.16	1.68
313	5.70	2.39
318	7.86	3.37
$E_a \text{ (kJ mol}^{-1}\text{)}$	51.14	55.99
$\Delta H^\ddagger \text{ (kJ mol}^{-1}\text{)}$	47.88	56.61
$\Delta S^\ddagger \text{ (JK}^{-1} \text{ mol}^{-1}\text{)}$	-118.08	-97.99
$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)}$	84.55	87.03

## Conclusion

In PBC mediated oxidation of acetyl acetone and benzoyl acetone,  $\alpha$ -C-H bond is ruptured to yield corresponding triones as the main products. The stoichiometry was assigned as 2:3. Both the diketones exhibited reaction mechanisms of the protonated and non-protonated PBC species forming cyclic chromate ester as an intermediate at pre-equilibrium state. The reaction proceeds via participation of enol form of diketone showing fraction-order kinetics each with ketone and H<sup>+</sup> ion.

## Acknowledgement

Thanks are due to the Principal and Head, Chemistry Department, S.G.S. Govt. P.G. College, Sidhi (M.P.) for providing laboratory facility.

## Conflict of Interest

The authors declare conflict of no interest whatsoever.

## REFERENCES

- [1]. Corey, E.J. and Suggs, W.J. : Tetrahedron Lett., 1975, 2647,
- [2]. Chandra Surya, P., Suri, Deepa, Kothari, Seema, and Banerji, Kalyan K. : CSIR India, John Wiley and Sons Inc., 1998, 285-290.
- [3]. Cristau, H.J., Torreilles, E., Morand, P. and Cristol, H. : Tet. Lett., 1986, 1775.
- [4]. Khan, Chandani, R., Sharma, P.K. and Banerji, K.K. : J. Chem. Res. (S), 1995, 432, (M) 2622.
- [5]. Pareek, A., Kothari, S. and Banerji, K.K. : Int. J. Chem., 1995, 34B, 968.
- [6]. Aparna, P., Kothari, S. and Banerji, K.K. : J. Chem. Res. (S), 1994, 367, (M) 2133.
- [7]. Grover, A., Varshaney, S. and Banerji, K.K. : J. Chem., 1994, 33A, 622.

- [8]. Rathore, S., Sharma, P.K. and Banerji, K.K. : J. Chem. Res. (S), 1994, 504.
- [9]. Khan, M.U., Nigam, S.K., Nigam, A., Verma, J.K. and Chauhan, R.P.S.: Oxid. Commun., 2004, 22(1), 105-115.
- [10]. Nigam, S.K., Patel, Priyanka, Tiwari, A.K,S. and Tiwari, Anita : Nano vision, 2013, 3(2), 70-74.
- [11]. Saket, Ravendra, Sharma, K.N., and Dwivedi, Arvind Prasad : Int. J. Adv. Res. Chem. Sci., 2019, 6(3), 1-5.
- [12]. Sahu, Umakant, and Manikpuri, Nagmani ; Int. J. Sci. Dev. & Res., 2023, 8(4), 883-887.
- [13]. Kushwaha, Sarita, and Pradhan, Manisha : Int. J. Res. Trends and Innov., 2023, 8(1), 302-305.
- [14]. Kushwaha, Sarita, and Pradhan, Manisha : Int. J. Sci. Development and Res. 2023, 8(1), 1224-1227.
- [15]. Narayanan, N. and Balasubramanian, T.R. : Ind. J. Chem., 1986, 25B, 228.
- [16]. Perrin, D.D., Armarego, W.L. and Perrin, D.R. : "Purification of organic compounds" Pergamon Press, Oxford, 1966.
- [17]. Wiberg, K.B. : Oxidation of organic chemistry: Part-A, Academic Press, Newyork, 1965, p. 69.
- [18]. Rao, C.N.R. : "A Hand book of Physics and Chemistry", Affiliated Press, New Delhi, 1967, p. 169.
- [19]. Deno, Klanning, and Symons, M.C.R. and Newman, M.S. : J. Am. Chem. Soc., 1961, 32604.