Study of Oxidation of Diketones by Quinolinium Dichromate

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Abstract: In this perspective, the oxidation of acetyl acetone (AA) and benzoyl acetone (BA) in aqueous acetic acid in presence of mineral acid by QDC leads to the formation of corresponding pentane-2,3,4-tione and 1-phenyl butane-1,2,3-trione. The reaction follows first-order kinetic in low concentration of QDC. The rate varies direct proportionality to low concentrations of diketones, which tends to become, zero order at its higher concentrations. The catalytic data of rate is satisfied for the first-order in H^+ ion. The stoichiometry (2:3) was measured for the reactions. The protonated form of QDC species attacks at enolic form of organic substrate. The activation parameters and rate law of the oxidation reactions were derived that suggested the plausible reaction mechanism.

Key words: Oxidation, Kinetics, Quinolinium dichromate, acetyl acetone, benzoyl acetone.

1. INTRODUCTION

The chemical change occurring by redox process are of great academic and technical importance. Transition metals in higher oxidation state can generally be stabilized by charge delocalisation. A highly toxic[1] chromium (VI) compounds are converted into environmental friendly non-toxic chromium (III) by quinolinium dichromate (QDC) oxidant in an appropriate pH value medium. The oxidation of a few of organic compounds ethylene glycol,[2] cyclohexane diol,[3] 2-furfaldehydes,[4] and arsenic(II),[5] and metals in higher oxidation state by QDC has also been probed, but no further information on the kinetic is available.[6] Because Cr(VI) is in the highest oxidation state and the rection is complicated in such a rection system.

The active methylene compounds flanked by two carbonyl groups are supported to be backbone of synthetic chemistry. They exhibit tautomeric phenomenon and have ability to form complex with reacting species of oxidant and acquire extra stability due to chelation and intramolecular hydrogen bonding. It shows resonance which make $-CH_2-$ group more reactive and enolization proceeds $>C=O$ group and de-protonation of α-C-H of the conjugate of acid. Some excellent reviews on the exploration of reaction path ways already exist for diketones with different oxidants (Tl(III),[7] NDC,[8] IQBC,[9] NCSA,[10] SeO_2,[11] etc.). It is important to have further such investigation which will certainly provides us with more kinetic parameters and theoretical foundation for the design of reaction route in the organic synthesis and quantitative analysis of analytical chemistry. In this paper the results of kinetic studies of oxidation of acetyl acetone (AA) and benzoyl acetone (BA) by Quinolinium dichromate QDC is presented.

EXPERIMENTAL

Materials- QDC was synthesized and its solution was prepared in twice distilled water and mineral acid and standardized iodometrically as per method mentioned in literature.[12] All diketones (acetyl acetone, A.G. grade, benzoyl acetone, E-Merck) were used after distillation under reduced pressure.

All other reagent's (A.R. grade) standard solutions were prepared with double distilled water. The stoppered glass vessels (pyrex) and apparatus were used for the kinetic measurements.

The reactions were carried out in stoppered glass vessels in a thermos stated ($\pm 0.1^0$C) water bath. The reaction was initiated by adding QDC solution to a mixture containing diketones, H^+, acetic acid etc. both solutions being equilibrated at 308 K unless stated otherwise. After suitable intervals aliquot portions (2 cm^3) were analyzed iodometrically for QDC. The values of pseudo first-order rate constant (k_{obs}) were derived using integrated and graphical methods (plot of log [QDC] vs. time). The rates of duplicate runs were reproductible to $\pm 4\%$.

Results and Discussion

The data for kinetic and thermodynamic parameters were obtained for all diketones. The results are almost similar hence a few representative data are reproduced here.

Stoichiometry and products

The stoichiometry was determined with an excess of [QDC] over [diketone] under experimental conditions. The molar ratio of [reductant]/ [oxidant] as 2:3 could be established iodometrically. The reaction occurred as in equation (1)
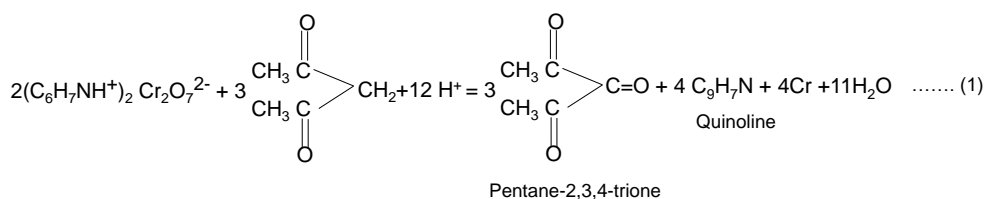
Pentane-2,3,4-trione

The corresponding products penten-2,3,4-trione and 1-phenyl, butane-1,2,3-trione were determined by transforming their 2,3-DNP derivatives. The addition of acrylonitrile/ butylated hydroxy toluene (BHT) did not affect the rate indicating that one electron oxidation is unlikely in the present reaction under the conditions of [diketone] >> [QDC], the plots of ln [QDC] against time is linear showing that reacting is first-order rate constants (k_{obs}) were determined by the integration method for seven values. The slope was evaluated almost as unity.

The rate constant (k_{obs}) was measured under fixed condition of [QDC] [H^+], ionic strength (μ) and temperature. The first-order values of rate constant were increased with an increase in [reductant] but at its higher concentration order declines i.e. fraction-order kinetics was observed with respect to [substrate] (Table 1) for the plots k vs. [substrate] passed through the origin grid and then bonds towards X-axis (Fig. 1). This shows complex formation between protonated species of oxidant and enolic substrate at pre-equilibrium state.

Table 1: Rate constants for the variation of concentration of di-ketones at 308 K

$10^3 \times$ [QDC] (mol dm^{-3}) = 3.33 (1, 2) ; [H^+] (mol dm^{-3}) = 0.125 (1), 0.166 (2) ;
CH$_3$COOH-H$_2$O %, (v/v) = 40 : 60 (1, 2)

$10^2 \times$[diketone] (mol dm^{-3})	Acetylacetone (AA)	Benzoyl acetone (BA)
1.25	1.41	-
1.50	-	1.43
1.66	-	-
2.00	2.11	1.86
2.50	2.63	2.30
3.33	3.52	2.81
5.00	4.21	3.54
6.00	-	3.40
6.66	4.71	-

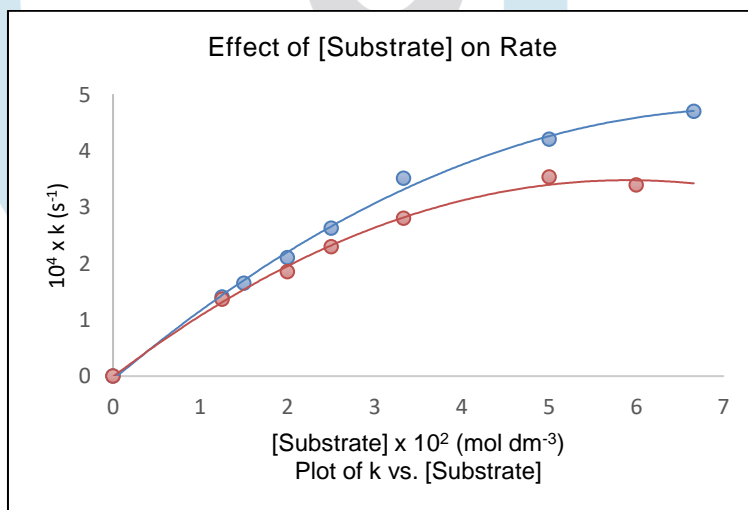Fig. 1 10^3 [QDC] (mol dm^{-3}) = 3.33 (1, 2) ;
[H^+] (mol dm^{-3}) = 0.125 (1), 0.166 (2) ;
CH$_3$COOH-H$_2$O %, (v/v) = 40:60 (1, 2)

The hydrogen ion conce... ...nditions of the reaction (Table 2). The rate enhances with increase in [H^+] and ... ... that first-order reaction is acid catalysed (Fig. 2).

Table 2: Dependence of the reaction rate on hydrogen ion concentration at 308 K

$10^3 \times$ [QDC] (mol dm^{-3}) = 3.33 (1, 2) ; $10^2 \times$ [diketone] (mol dm^{-3}) = 2.50 (1, 2) ;
CH$_3$COOH-H$_2$O %, (v/v) = 40 : 60 (1, 2)

[H^+] (mol dm^{-3})	Acetylacetone (AA)	Benzoyl acetone (BA)
0.050	1.45	-
0.100	2.64	1.46
0.125	2.52	1.71
0.166	-	2.30
0.200	5.49	2.82
0.250	6.70	3.41
0.333	-	4.75
0.400	-	5.50
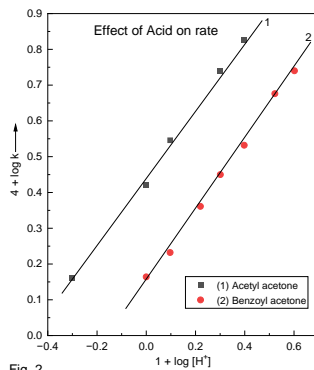
Fig. 2
Plot of log k vs. log [H⁺]

10^3 x [QDC] (mol dm^{-3}) = 3.33 (1,2) ;
10^2 x [diketone] (mol dm^{-3}) = 2.50 (1,2) ;
CH$_3$COOH-H$_2$O %, (v/v) = 40 : 60 (1, 2)

In this case, there is a possibility of positive ionic reactant, as the enhancement of the rate occur with the decreasing dielectric constant of the medium.[13] Due to polar nature of the solvent i.e. the polar solvent molecules surround the transition state and result in less disproportion. The rate of reaction remains almost unchanged while raising the [NaCl]. It proves that the interaction in rate determining step is not of ion-ion type.[14]

Reaction mechanism

On the basis of the above results and the information about intermediate complexes, the mechanism may be proposed as a mode :

The protonated $(QOH^+)_2\ Cr_2O_5 + H^+ \xrightarrow{K_1}$ ... (2)
QDC

K_2

Enol (AA)

Cr(VI) + Cr(IV) $\xrightarrow{fast}$ 2 Cr(V) ... (6)

Z Cr(V) + 2 reductant enol $\xrightarrow{fast}$ Cr(III) + 3 H$_2$O + 2 ... (7)

Acid dependent path

The rate law
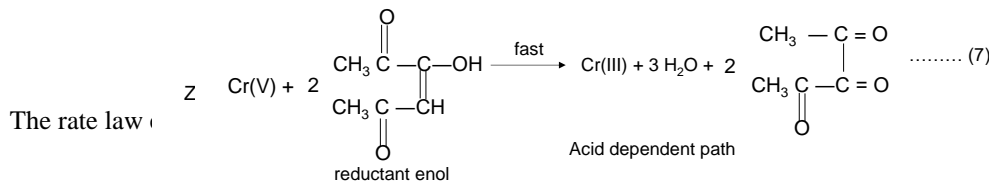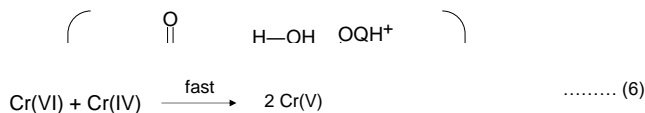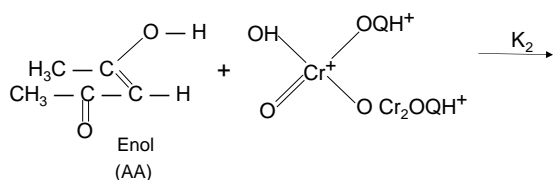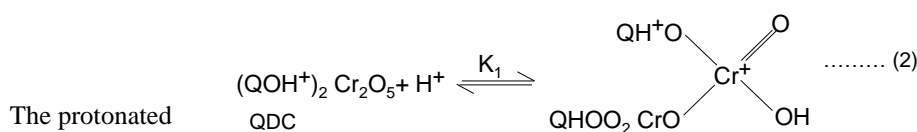
Transforming equation (8) in the form of equation (9)

$$k_{obs}^{-1} = \frac{1}{k\,K_1 K_2 [H^+][Enol\ (substrate)]} + \frac{1}{k} \quad \ldots\ldots (9)$$

The Michaelis-Menten equation is validated by equation (9)
The observed order of reactivity is found as :

Acetyl acetone > benzoyl acetone

Due to strem electronegative character of group, the cleavage of α-C-H occurs and loss of α-H- atom as proton is caused in the present series of compounds. The -CH$_2$- group lies between two moiety observes rapid enolization by intramolecular hydrogen bonding.

The bulky design of benzoyl acetone, presence of sufficient more enolic content, ability to form chelating ring showing steric hinderance are the main reason of slower rate of benzoyl acetone than acetyl acetone.

The activation (Eᵃ) is acetyl acetone is lower than benzoyl acetone (Table 3). The solvation of rigid activated complex at transition states observed loss of entropy of activation and reduce randomness of the molecules limits translational and rotational degree of freedom. The values of Gibbs free energy ΔG# lies in close vicinity assessing similar mechanism operative. The observation of reactivity indicated that the electron releasing group increases the oxidation process. Overall assessment of the reaction is found enthalpy controlled.

Table 3: Activation parameters of the oxidation of diketones- QDC complex

D-ketone	Ea	ΔH#	ΔG#	−ΔS#

	(kJ mol^{-1})	(kJ mol^{-1})	(kJ mol^{-1})	(Jmol^{-1} K^{-1})
Acetyl acetone	53.68	50.70	87.55	118.67
Benzoyl acetone	56.75	52.53	87.84	113.71

Conclusions

The study reveals first-order kinetics with respect to Quinolinium dichromate and explains complex formation that follows stoichiometry 2:3. Triones were isolated as reaction products. Reaction was found acid catalysed and protonated species of QDC participates in reaction mechanism. The order of reactivity was discussed based on some physical and thermodynamic parameters. The rate law was relevant to illustrated mechanism.

Acknowledgement

Conflict of Interest

There are no conflicts to declare.

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