Kinetic Study of Oxidation of Benzoyl Acetone by NDC

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ABSTRACT The oxidation of benzoyl acetone has been carried out with Nicotinium dichromate in acetic acid medium in the presence of H ion. It is found that rate is a direct function of first power concentration of oxidant i.e. NDC and zero order with respect to substrate i.e. active methylene compound. The reaction was found to increase with increase. concentration of acid. The reactive species is H_2CrO_4.

Nicotinium dichromate is a titrant for the oxidimetric determination of some typical active methylene compound like benzoyl acetone in acidic medium. This chromium (V1) complex of heterocyclic bases is a mild oxidant, soluble in organic solvent and used under anhydrous condition[1] . It is a new oxidant, non-hygroscopic, non-photosensitive stable yellow orange solid[2]. Kinetic and mechanistic studies of oxidation by chromium (VI) complexes like PFC, QFC PCC, QCC, BPCC, PBC, and BPC are common and the oxidation is first order with respect to chromium (VI) reagent and is catalyzed by mineral acid.

While the oxidation of active methylene compound by NDC is very rare and scanty and none of the researcher acclaimed the use of NDC in probing the oxidation kinetics of active methylene compound with it, thus we have chosen NDC for the first time as an oxidant for the kinetics study of active methylene compounds in aqueous acetic acid medium.

Oxidation of active methylene compound is also shown by other oxidants like Bromamine-B (BAB)[3], perox-omon-opho-sphoric acid (PMPA)[4], Ce(IV)[5], Mn (II)[6], MnO_4^-[7] etc. But good results are obtained by using NDC in aqueous acetic acid medium.

OBSERVATIONAL ANALYSIS
Active methylene compound employed are commercially available (sigma). All other chemicals used were AnalaR grade. The stock solution of the substrate was prepared in purified glacial acetic acid-water mixture as required. The standard solution of NDC was obtained by dissolving weighed quantity of NDC in 100% acetic acid. The standardization is done iodometrically.

The kinetic measurements were made under pseudo first order condition by maintaining (substrate) >> (oxidant). The reaction was initiated by adding requisite amount of solution of substrate to the NDC solution containing acetic acid and water both being equilibrated in a thermostatic bath. The unreacted NDC was estimated iodometrically. The duplicate kinetic runs showed reproducible results of rate constant within $\pm$2%.

RESULT AND DISCUSSION
The stoichiomeitric data established that for complete oxidation of 3 moles of each benzoyl acetone and one mole of NDC is required. The product of the oxidation was ascertained by the formation of 2, 4-diphenyl hydrazone (DNP) using 2, 4-dinitrophenyl hydrazine[8].The kinetic data have been collected for 5 fold concentration of oxidant (NDC) at fixed concentration

of other reactants and temperature. The linear plot of log a/(a-x) vs. time shows the first-order rate dependency with respect to NDC.

Typical kinetic run for the effect of Nicotinium dichromate
Kinetics of oxidation reaction between benzoyl acetone with NDC

[B.A.] = 1.25 ×10^{-2} (mol.dm^{-3}), [NDC] = 2.50 ×10^{-3} (mol.dm^{-3}),
[H^+] = 1.25 ×10^{-3} (mol.dm^{-3}),   HOAc-H_2O = 15 % (v/V)
Temp. = 308 ^{0}k.

Table: 1

S.No.	Time (sec.)	Vol. of N / 1000 hypo ml.	$10_4 k_1 (s^{-1})$
1.	0	5.00	-
2.	420	4.10	4.725
3.	840	3.35	4.768
4.	1260	2.80	4.602
5.	1680	2.30	4.623
6.	2100	1.85	4.735
7.	2520	1.55	4.648
8.	2940	1.25	4.716

Average k^1 = 4.682×10^{-4}(s^{-1})
Graphical k_1 = 4.747×10^{-4} (s^{-1})

The reaction follows first-order kinetics with respect to substrate at lower concentration and tends toward zero-order at higher concentration. The evidence indicates the formation of complex during the reaction between each substrate and oxidant. The plot of k_1 vs. [H^2SO^4] was linear with the positive unit slope and passing through origin which led to the conclusion that reaction is fully acid catalyzed and first-order with respect to acid concentration Fig. II.
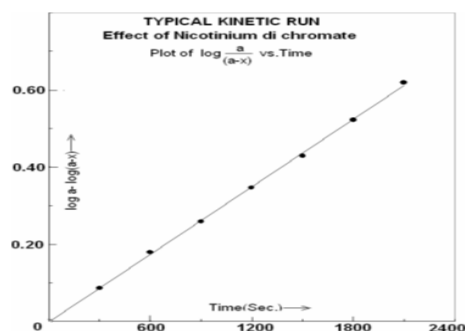

Fig. I : [B.A.] = 1.25 ×10^{-2} (mol.dm^{-3}), [NDC] = 2.50 ×10^{-3} (mol.dm^{-3}),

$[H^+]$ = 1.25 $\times 10^{-3}$ (mol.dm^{-3}), HOAc-H$_2$O =15 % (v/V), Temp. = 308 K

Kinetics of oxidation reaction between benzoyl acetone with NDC
[B.A.] = 1.25 $\times 10^{-2}$ (mol.dm^{-3}), [NDC] =2.50 $\times 10^{-3}$ (mol.dm^{-3}), $[H^+]$ = 2.00 $\times 10^{-3}$ (mol.dm^{-3}), HOAc-H$_2$O = 15 % (v/V),Temp.=308K

Table: 2
Typical kinetic run for the effect of Sulphuric acid

S.No.	Time (sec.)	Vol. of N / 1000 hypo ml.	$10_4 k_1 (s^{-1})$
1.	0	5.00	-
2.	300	4.10	6.616
3.	600	3.35	6.675
4.	900	2.75	6.643
5.	1200	2.25	6.655
6.	1500	1.85	6.629
7.	1800	1.50	6.689
8.	2100	1.20	6.797

Ave average k_1 = 6.676$\times 10^{-4}$(s^{-1}),
Graphical k_1 = 6.641$\times 10^{-4}$(s^{-1})

The polarity of the medium[9] was varied by using different percentage of acetic acid and water binary mixture. It was observed that the rate of oxidation of substrate increase with increase in the percentage composition i.e. content of acetic acid in the reaction mixture. Since the plot of log k_1 vs. 1/D is linear with positive slop.

Fig. II: [B.A.] = 1.25 $\times 10^{-2}$ (mol.dm^{-3}), [NDC] = 2.50 $\times 10^{-3}$ (mol.dm^{-3}),
$[H^+]$ = 2.00 $\times 10^{-3}$ (mol.dm^{-3}), HOAc-H$_2$O = 15 % (v/V), Temp. = 308 ^{0}k.

The addition of primary salts does not alter the rate of reaction. This shows that rate determining step involves either neutral species or an ion and a neutral molecule. The study rules out the formation of any free radical by the addition of acrylonitrile. H2CrO4 is thought to be the oxidizing species since the rate of the reaction increase with increasing chromic acid concentration. This can be explained by the following equilibrium.

$$H_2CrO_4 \rightleftharpoons H\,CrO^-_4 + H^+$$

In the presence of acid, the equilibrium will shift to the left and hence all the chromic acid must be present as H2CrO4. This concludes that H2CrO4 is the oxidizing species in the oxidation of active methylene compound by NDC.

Mechanism
The probable mechanism for the oxidation of active methylene compounds in aqueous acetic medium can therefore be formulated as

The above mechanism leads to the following rate law.

$$k_{obs} = \frac{Rate}{[NDC]_T} = \frac{k_1 k_2 k [Enol] [H^+]}{[\text{Nicotinic acid}] k_1 + k_1 [H^+] + k_1 k_2 [Enol] + [H^+]}$$

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