Study of NDC and Diethyl Malonate "The Kinetic and oxidative Approach"

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ABSTRACT *The oxidation of diethyl malonate has been carried out with Nicotinium dichromate in acetic acid medium in the presence of hydrogen 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.diethyl malonate. The reaction was found to increase with increase. concentration of acid. The reactive species is H_2CrO_4*

INTRODUCTION

Nicotinium dichromate is a titrant for the oxidimetric determination of some typical active methylene compound 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.The principles of chemical kinetics apply[3]

While the oxidation of DEM 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], peroxomonophosphoric 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.

EXPERIMENT

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 +2%.

RESULT AND DISCUSSION

The stoichiometric data established that for complete oxidation of 3 moles of DEM and one mole of NDC is required. The product of the oxidation was ascertained by the formation of Meso oxalic acid using0.5% of B, B-di mapthol in concentrated sulphuric acid[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.
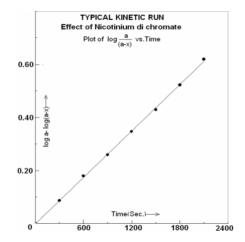

Fig. I: $[DEM.] = 1.25 \times 10^{-2}$ $(mol.dm^{-3})$, $[NDC] = 2.50 \times 10^{-3}$ $(mol.dm^{-3})$, $[H^+] = 1.25 \times 10^{-3}$ $(mol.dm^{-3})$, $HOAc-H_2O = 15\%$ (v/V), $Temp. = 308$ K

Table: 1 Typical kinetic run for the effect of Nicotinium dichromate

Kinetics of oxidation reaction between di ethyl Malonate with NDC
$[DEM] = 2.00 \times 10^{-2}$ $(mol.dm^{-3})$, $[NDC] = 2.50 \times 10^{-3}$ $(mol.dm^{-3})$, $[H^+] = 2.00 \times 10^{-3}$ $(mol.dm^{-3})$, $HOAc-H_2O = 15\%$ (v/V)
$Temp. = 308$ ^0k.

S.No.	Time (sec.)	Vol. of N / 1000 hypo ml.	10_4 k_1 (s^{-1})
1.	0	5.00	-
2.	600	3.90	2.070
3.	1200	3.05	2.059
4.	1800	2.45	1.918
5.	2400	1.95	2.016
6.	3000	1.45	2.063
7.	3600	1.10	2.103
8.	4200	0.85	2.109

Average $k_1 = 2.057 \times 10^{-4} (s^{-1})$
Graphical $k_1 = 2.055 \times 10^{-4} (s^{-1})$

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.

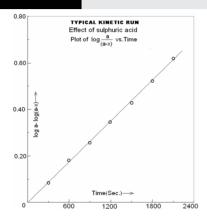**Fig. II:** $[DEM] = 1.25 \times 10^{-2} \, (mol.dm^{-3})$, $[NDC] = 2.50 \times 10^{-3} \, (mol.dm^{-3})$, $[H^+] = 2.00 \times 10^{-3} \, (mol.dm^{-3})$, HOAc-$H_2O$ = 15 % (v/V), Temp. = 308 ^{0}k.

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.

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. H_2CrO_4 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.

In the presence of acid, the equilibrium will shift to the left and hence all the chromic acid must be present as H_2CrO_4. This concludes that H_2CrO_4 is the oxidizing species in the oxidation of diethyl malonate by NDC.

Mechanism

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

(Oxidant product)

The above mechanism leads to the following rate law.

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

REFERENCES
1. W.Z.Moore"Basic Physics Chemistry"university of Sydney,IInd aEdn. P.227(1989)
2. G. Cainelli and G. Cardillio, Chromium oxidation in organic chemistry, pp. 40-258 Springer-Verlage, Berline, 1984
3. Lopaz ,A.Gonzalez.F.P.Cossio,and Palomo :Synth ,Commun.15,1197-1211.(1985)
4. T..Asha, Lyanger, D.S. Mahadevappa and Puttaswami:Proc. Indian Acad. Sci. (Chem. Sci.) Vol.104, No.PP . 611-618(1992)
5. Chakrapani p.,S.N. mahapatta, Akhil K. Panigrahi,Radhashyam S, Panda: bull. Soc.jpn.60.3391-3395(Sept.1997)
6. R.K.Prasad ,S.N.Tripathi :Indian J. chem,19A,340 (1980)
7. M.Mrakavova,and L.Treindal :Chem,Zvesti,36,785(1982
8. F.G. mann and B.C. Sunders :Practical Organic Chemistry 4Th Edition Long Mann,pp.261-262(1960)
9. N.Bjerrum: "Elementry practical Organic Chemistry" Part-III second addition pp. 118(1974)
10. J.N. bronsted :J.Phy.chem.102,169(1922). J.P.Sewanee, Anita valechha:j.Indian Chem. Soc.,70-76(1993)
11. J.P.Sewanee,Anita Valechha,Alka SinghAnd N.D.Valechha:J.indian Chem.Sco.,70-76(1993)