



Kinetic Study of Oxidation of ethyl aceto acetate by NDC

KEYWORDS

Oxidimetric, Degradation, Nicotinium dichromate.

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ABSTRACT

The oxidation of Ethyl aceto acetate(EAA) 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. EAA. The reaction was found to increase with increase concentration of acid. The reactive species is H₂CrO₄.

INTRODUCTION

Nicotinium dichromate is a titrant for the oxidimetric determination of Ethyl aceto acetate compound in acidic medium. This chromium (VI) complex of heterocyclic bases is a mild oxidant, soluble in organic solvent and used under anhydrous condition¹. It is a new oxidant, non-hygroscopic, non-photosensitive stable yellow orange solid². 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 ethyl aceto acetate compound by NDC is very rare and scanty and none of the researcher acclaimed the use of NDC in probing the oxidation kinetics of ethyl aceto acetate 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 EAA is also shown by other oxidants like Bromamine-B (BAB)³, peroxomonophosphoric acid (PMPA)⁴, Ce(IV)⁵, Mn (II)⁶, MnO⁻⁴⁷ etc. But good results are obtained by using NDC in aqueous acetic acid medium.

EXPERIMENT

EAA 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 each EAA compound and one mole of NDC is required. The product of the oxidation was ascertained by the formation of alpha-beta-diketo buteric acid using semicarbazide hydrochloride^{8,9}. 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.

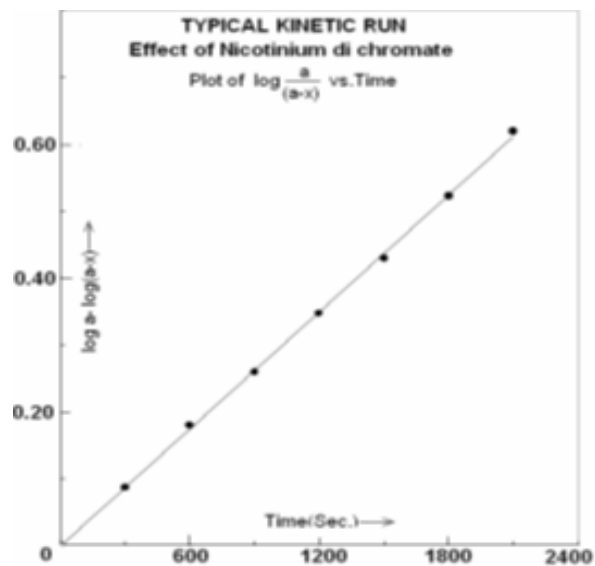


Fig.1: [E.A.A.] = 1.25×10^{-2} (mol.dm⁻³), [NDC] = 2.50×10^{-3} (mol.dm⁻³), [H⁺] = 1.25×10^{-3} (mol.dm⁻³), HOAc-H₂O = 15% (v/v), Temp. = 308 K

Table: 1 Typical kinetic run for the effect of Nicotinium dichromate Kinetics of oxidation reaction between EAA with NDC [E.A.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-H₂O = 15% (v/v) Temp. = 308 K.

S.No.	Time (sec.)	Vol. of N / 1000 hypo ml.	104 k1 (s ⁻¹)
1.	0	5.00	-
2.	900	4.05	2.341
3.	1800	3.30	2.308
4.	2700	2.65	2.351
5.	3600	2.15	0.344
6.	4500	1.80	2.468
7.	5400	1.45	2.292
8.	6300	1.15	2.333

Average k₁ = 2.352×10^{-4} (s⁻¹)
Graphical k₁ = 2.346×10^{-4} (s⁻¹)

The reaction follows first-order kinetics with respect to substrate at lower concentration and tends toward zero-order at higher

concentration

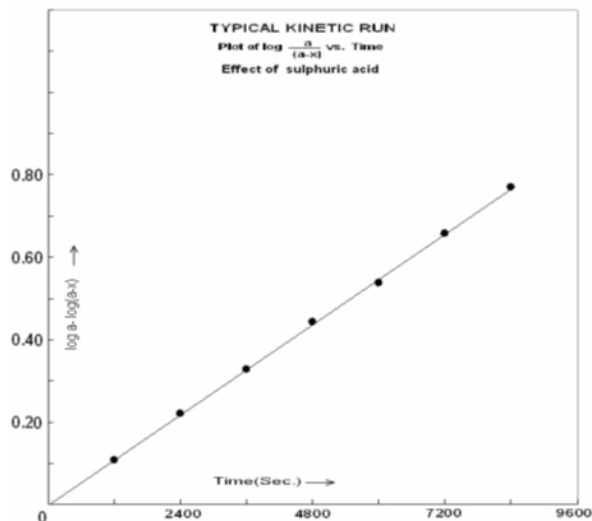


Fig. II: [E.A.A.] = 1.25×10^{-2} (mol.dm⁻³), [NDC] = 2.50×10^{-3} (mol.dm⁻³), [H⁺] = 2.00×10^{-3} (mol.dm⁻³), HOAc-H₂O = 15% (v/v), Temp. = 308K.

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

Kinetics of oxidation reaction between EAA with NDC
 [E.A.A.] = 1.25×10^{-2} (mol.dm⁻³), [NDC] = 2.50×10^{-3} (mol.dm⁻³),
 [H⁺] = 2.00×10^{-3} (mol.dm⁻³), HOAc-H₂O = 15% (v/v), Temp. = 308K

S.No.	Time (sec.)	Vol. of N / 1000 hypo ml.	104 k1 (s-1)
1.	0	5.00	-
2.	1200	3.90	2.070
3.	2400	3.05	2.059
4.	3600	2.40	2.039
5.	4800	1.90	2.016
6.	6000	1.45	2.063
7.	7200	1.10	2.103
8.	8400	0.85	2.109

Average $k_1 = 2.2065 \times 10^{-4}$ (s⁻¹),
 Graphical $k_1 = 2.059 \times 10^{-4}$ (s⁻¹)

The polarity of the medium 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 k1 vs. 1/D is linear with positive slope.

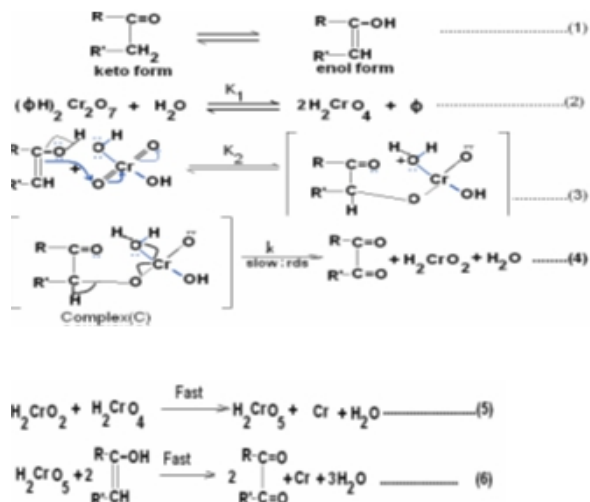
The addition of primary salts does not alter the rate of reaction. This shows that rate determining step involves either neutral species or an ion and a neutral molecule. The study rules out the formation of any free radical by the addition of acrylonitrile. H₂CrO₄ is thought to be the oxidizing species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



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 EAA by NDC.

Mechanism

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



(Oxidant product)

The above mechanism leads to the following rate law.

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

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