



Studies on substituent effect on the oxidation kinetics of Acetophenones by acid dichromate

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Abstract: Kinetics of the oxidation of acetophenone and some of its para substituted derivatives by acidic dichromate has been investigated in acetic acid-water medium. The reaction shows first order dependence on [oxidant] and fractional order dependence on [substrate]. Benzoic acid and substituted benzoic acids were formed as the product which was proved by melting point determination and IR spectral analysis. Electron withdrawing substituents accelerate the rate of reaction while electron donating substituents retard the rate. The rate data obey Hammett's relationship. The reaction does not induce the polymerisation of added acrylonitrile which rules out the involvement of free radicals in the reaction. The effect of solvent composition shows that the rate increases with decrease in dielectric constant of the medium. Activation parameters have been evaluated and a mechanism in consistent with the obtained kinetic results have been proposed.

Key words : Acetophenone, oxidation, kinetics, mechanism, acidic dichromate.

Introduction

Oxidation of organic compounds is very important and found useful in chemical industries for the production of various commercial products. Most of the industrially important organic compounds like aldehydes, ketones, carboxylic acids etc. can be produced by the oxidation of related substrates by various oxidizing agents¹⁻². Permanganate, chromate, hypochlorite etc. are extensively used for the primary and secondary alcohol oxidation reactions in a selective manner to get corresponding aldehydes³⁻⁵. Kinetic studies on the oxidation of alcohols using permanganate and chromate were already reported⁶⁻¹¹. But only few reports are available on the kinetics of oxidation of ketones by dichromate as oxidant and hence we carried out this work¹²⁻¹³.

The present paper reports the kinetics and mechanism of the oxidation of acetophenone and its para substituted derivatives in aqueous acetic acid medium using potassium dichromate. Stoichiometry of the reaction, isolation of product and its characterization, effect of oxidant and substrate concentration, effect of dielectric constant of the medium, effect of added salt and temperature on the reaction rate are carried out. Effect of substituents on the rate of oxidation was also carried out by using para substituted acetophenones. Thermodynamic variables like energy of activation (E_a), enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger) were calculated and a suitable mechanism is suggested in accordance with the experimental observations.

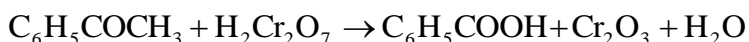
Experimental

Potassium dichromate (AR, E Merck, India) was used and its solution was prepared in doubly distilled water. Acetic acid (E Merck, India) was purified by refluxing with potassium dichromate for about three hours and distilled¹⁴⁻¹⁵. Analar grade acetophenone (Merck KGaA, Germany) was used after distillation. p-chloro, p-nitro and p-methyl and p-methoxy acetophenones (SRL, India and Merck KGaA, Germany) were used as such.

Kinetic investigations were carried out under the condition [acetophenone] >> [dichromate] in presence of 2.0 mol dm⁻³ H₂SO₄. Reaction progress was measured by spectrophotometrically by using Hitachi U-3000 UV-Visible spectrophotometer. The experiments were repeated and pseudo-first order rate constants, k_{obs} were determined from the linear least square plots of log [dichromate] versus time.

Results and Discussion

Stoichiometric analysis was conducted under the condition [dichromate] >> [acetophenone] till the completion of reaction. It was proved that one mole of dichromate is equivalent to one mole of acetophenone.



Benzoic acid and corresponding substituted benzoic acids were obtained as the product with very high yield (> 90%). The products were characterized by melting point and infra red spectral analysis. The melting points of the products are given in the table I and the infra red spectrum of the product of oxidation of acetophenone is given in figure 1.

Table 1. Melting point of products on oxidation of acetophenone and substituted acetophenones

Sl. No.	Substrate	Melting point of product (°C)
1	Acetophenone	119 ± 2
2	4-chloroacetophenone	238 ± 2
3	4-nitroacetophenone	236 ± 2
4	4-methoxyacetophenone	182 ± 2
5	4-methylacetophenone	181 ± 2

The obtained results of melting point were compared with that of authentic samples and found to be similar. This showed that the products formed may be corresponding acids. This was further confirmed by infra red spectral analysis by taking acetophenone as the typical substrate.

The infra red absorption spectrum was recorded from KBr pellets using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in Figure 1.

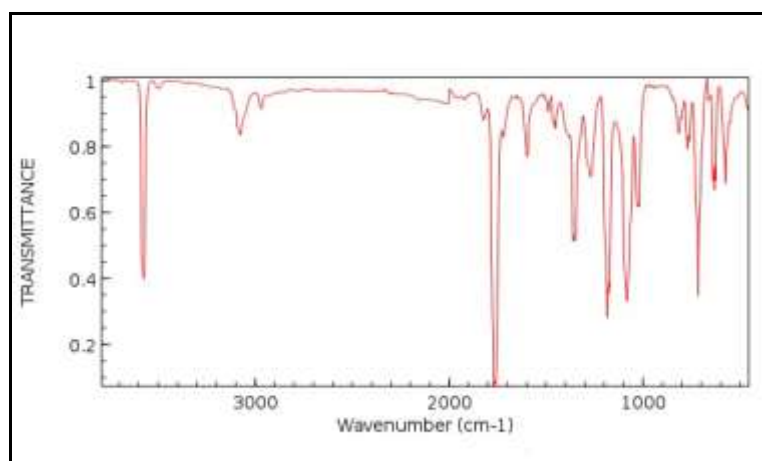


Fig.1: Infra red spectrum of the product

The infra red spectrum gave sharp peaks at 3350 cm^{-1} (O–H stretching), 1750 cm^{-1} (C=O stretching) and 1600 cm^{-1} (C=C stretching). Presence of these peaks leads to the conclusion that the product formed may be benzoic acid.

All these analyses, melting point determination and infra red spectral studies confirmed the formation of benzoic acid and substituted benzoic acids as the product on the oxidation of acetophenones by acid dichromate in aqueous medium.

The oxidation of acetophenone was carried out with different initial [dichromate] and [substrate] in 50% aqueous acetic acid medium at 303 K. The effect of concentration of both oxidant and substrate on oxidation of acetophenone is given in table 1. The logarithmic plot of [dichromate] versus time was found to be linear at various dichromate concentrations and these results proved the first order dependence of the reaction on [dichromate]. This was again proved from the constant values of specific rates (k_{obs}) for the different [dichromate] for a given [substrate]. The effect of concentration of substrate on reaction rate was followed by taking different initial [acetophenone] and the observed rate constant increased with [substrate] in a non linear fashion. The second order rate constants (k_2), were found to be varying with respect to [substrate] which indicates the fractional order dependence of the reaction with respect to the [substrate]. These results were given in Table 2.

Table 2: Effect of [oxidant] and [substrate] on the rate of oxidation of acetophenone

Temperature - 303 K

Medium - 50% aq. HOAc (v/v)

[Oxidant] x 10^3 (mol dm ⁻³)	[Substrate] x 10^2 (mol dm ⁻³)	k_{obs} x 10^5 (s ⁻¹)	k_2 x 10^3 (dm ³ mol ⁻¹ s ⁻¹)
2	2	4.78	2.39
1.5	2	4.93	2.47
1.0	2	4.86	2.43
0.5	2	4.96	2.48
2	2	4.78	2.39
2	5	8.22	1.64
2	3.5	11.51	1.53
2	4	12.79	1.28

The effect of dielectric constant of the medium on acetophenone oxidation was performed under pseudo first order condition, by varying the acetic acid percentage and is given in table 3. The reaction rate is increased with the increase in percentage of acetic acid (decrease in dielectric constant of the medium). This suggests the interaction between two dipoles ($\text{H}_2\text{Cr}_2\text{O}_7$ and enol form of acetophenone) or between the ion and a dipole (HCrO_4^- and enol form of acetophenone) to form a less polar transition state.

Table 3: Effect of dielectric constant of the medium on the rate of oxidation.

[Oxidant] x $10^3 = 2.0\text{ mol dm}^{-3}$ [Substrate] x $10^2 = 2.0\text{ mol dm}^{-3}$

Temperature - 303 K

Acetic acid : water	Dielectric constant	k_{obs} x 10^5 (s ⁻¹)	k_2 x 10^3 (dm ³ mol ⁻¹ s ⁻¹)
20 : 80	61	3.48	2.39
40 : 60	47	4.04	1.71
50 : 50	39.8	4.78	2.02
60 : 40	32.0	5.90	2.95
70 : 30	24.5	7.99	3.99

The effect of substituents on the rate of oxidation of acetophenone has been studied and is found in the order $p - \text{NO}_2 > p - \text{Cl} > \text{H} > p - \text{CH}_3 > p - \text{OCH}_3$. These results are presented in table 4. The electron-releasing substituents retard the oxidation process while the electron-withdrawing substituents accelerate the process.

Table 4: Effect of substituents on the rate of oxidation

[Oxidant] x 10³ = 2.0 mol dm⁻³ [Substrate] x 10² = 2.0 mol dm⁻³
 Medium - 50% aq. HOAc (v/v) Temperature - 303 K

Substrate	k _{obs} x 10 ⁵ (s ⁻¹)	k ₂ x 10 ³ (dm ³ mol ⁻¹ s ⁻¹)
p-nitro	15.8	7.90
p-chloro	10.2	5.10
H	4.78	2.39
p-methyl	4.08	2.04
p-mthoxy	3.58	1.79

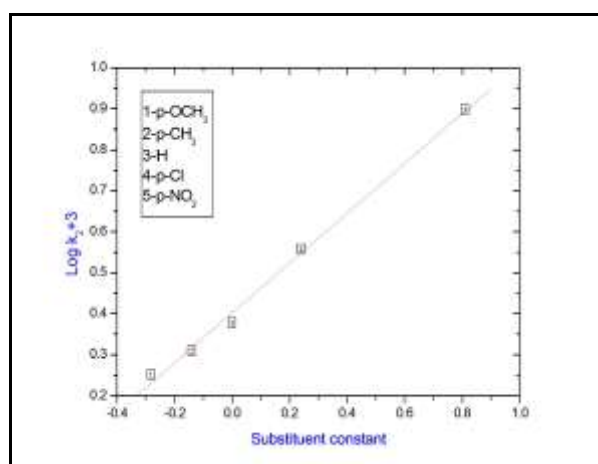
The effect of temperature on the rate of oxidation of acetophenone using dichromate in 50% aq. HOAc (v/v) was studied in the temperature range 303 K to 318 K. The values of various thermodynamic parameters were calculated and presented in table 5.

Table 5: Activation parameters for the oxidation of benzyl alcohols

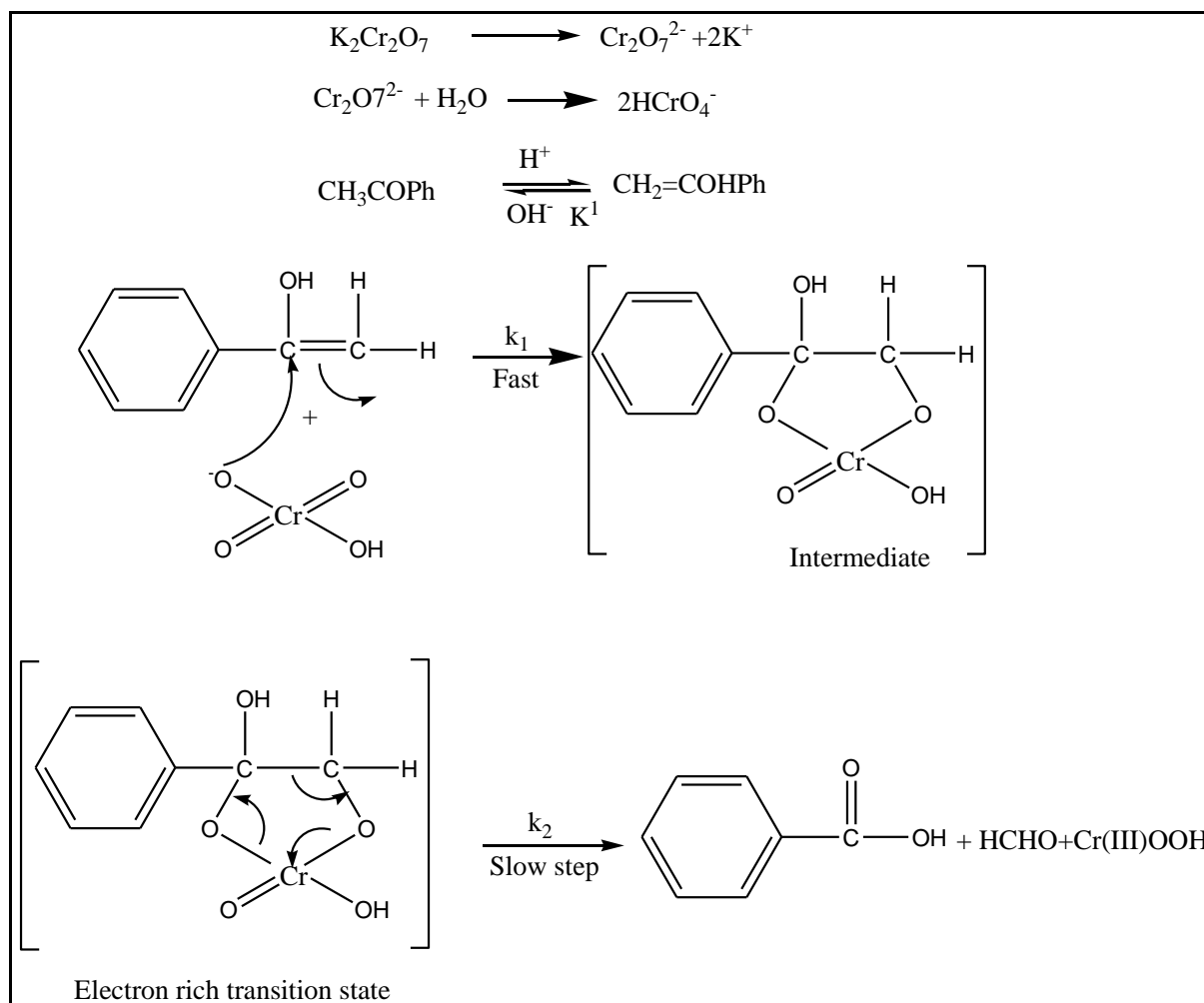
Medium - 50% aq. HOAc Temperature - 303 K

Substrate	k ₂ x10 ³ (dm ³ mol ⁻¹ s ⁻¹)	E _a (kJ mol ⁻¹)	ΔH [#] (kJ mol ⁻¹)	-ΔS [#] (JK ⁻¹ mol ⁻¹)	ΔG [#] (kJ mol ⁻¹)
Acetophenone	2.39	35.55	34.19	163.39	83.70

The oxidation of acetophenone by dichromate in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile and rules out the involvement of any radical intermediate in the reaction. The reaction was found to show first order kinetics with respect to [oxidant] and fractional order kinetics with [substrate]. The effect of polarity of the medium on the rate of oxidation of acetophenone was carried out by varying the acetic acid percentage in the reaction mixture. It has been observed that the reaction rate increases with increase in percentage of acetic acid (decrease in dielectric constant of the medium) suggesting more polar solvents may require larger reaction time. The plot of log k₂ versus 1/D, where D is the dielectric constant of the medium is linear (r = 0.9974) with a negative slope. This implies the occurrence of an interaction between a dipole and a negative ion and indicates the probable involvement of HCrO₄⁻ species in the reaction. The value of entropy of activation, ΔS[#] is negative indicating a large surrendering of disorder in the transition state and this is in agreement with the prediction of the formation of a stable intermediate. The influence of substituents at the para position of the benzene ring of acetophenone was studied and found that electron-releasing substituents retard the oxidation process while the electron-withdrawing groups accelerate the process. The plot of k₂ against σ, where σ is the substituent constant gives a positive slope indicating an electron rich carbon centre in the transition state (Figure 2)

**Fig.2: Hammett plot for the oxidation of acetophenones**

Based on the above facts the mechanism of the oxidation of acetophenone by dichromate may be suggested as follows. Dichromate in the aqueous acetic acid medium exists as HCrO_4^- as active species. Acetophenone undergoes keto-enol tautomerism and the enol form is the active species. The chromic acid or chromate undergoes pericyclic addition with the enol form of acetophenone to give a chromate ester by a fast equilibrium. The intermediate chromate ester undergoes decomposition through a transition state involving electron rich carbon centre which is stabilized by electron withdrawing groups. This is followed by rate determining slow decomposition of chromate ester giving benzoic acid as the final product. The proposed mechanism is given below.



The oxidation of acetophenone and its para substituted derivatives by dichromate in aqueous acetic acid medium gave corresponding acids as the product. A suitable mechanism involving the formation of a chromate ester which on decomposition gave corresponding acid is proposed. This method can be adopted to study the kinetics of other substrates to propose the mechanism of the reaction.

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