

Kinetics of Oxidative Hydrolysis of Oximes of Acetophenone and *Para* Substituted Acetophenone Oximes by Cr(VI) in Acetic Acid Medium

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The kinetics of oxidative hydrolysis of acetophenone oxime by Cr(VI) in 10% (v/v) N,N-dimethylformamide at different concentrations of acetic acid have been investigated. There is an increase (0.5-7.0 M) in the rate upto 3 M acetic acid concentration and slight decrease thereafter. A first order dependence on [oxime] and [HCrO₄] is observed. Effect of substituents gave a negative value (-0.83 for Hammett's reaction constant ρ).

INTRODUCTION

It is known that oxidants such as chromium(VI) have been used as oxidants for the preparation of the carbonyl compounds from their oximes through an oxidative hydrolytic reaction. No work was however reported in the literature on the kinetics of the oxidative hydrolysis of oximes with chromium(VI). Oximes of substituted acetophenones were used in these laboratories for the photometric determination of chromium(VI) and it was observed in these investigations that chromium(VI) is reduced to chromium(III) and the oxime is converted fast into the corresponding ketone. The kinetics of reduction of chromium(VI) in presence of the oximes of acetophenone and its *para* substituted compounds in acid solutions is therefore studied in acetic acid and the results obtained are presented here.

EXPERIMENTAL

The reaction is studied essentially under pseudo first order conditions keeping the concentration of chromium(VI) very much lower than the concentration of the substrate. The absorbance of chromium(VI) at 450 nm is read at different times to monitor the reaction. A suitable correction for the absorbance of chromium(III) at this wavelength. The product of the reaction, is made by subtracting the absorbance of chromium(III) measured at 450 nm from the measured absorbance of Cr(VI). The absorbance of chromium(III) at 450 nm in any particular instance is computed from the absorbance of chromium(III) under the specified experimental

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conditions at a wavelength different from 450 nm. This wavelength was selected on the basis of the following criteria.

1. There shall be no absorbance for chromium(VI) at this wavelength.
2. A definite stoichiometric relation shall exist between the absorbances of chromium(III) at this wavelength and at 450 nm.
3. Beer's law is applicable for chromium(III) at this wavelength under the experimental conditions.

These criteria are satisfied at a wavelength of 635 nm or a value near about this depending on the experimental conditions. Spectra of the reaction mixture are recorded immediately after mixing the components and also after a large interval of time (12 hrs) against water as the blank. Similar spectra are recorded with the reaction mixture devoid of the substrate to ascertain the reaction if any, between chromium(VI) and the other components of the reaction mixture. Typical spectra are presented at relevant places. A solution of the substrate in dimethylformamide is used in the studies since oximes are insoluble in water. The effect of concentration of the acid and at an optimum acid concentration, the effect of the concentration of chromium(VI), concentration of the substrate, temperature, organic co-solvent, metal ions (Cu^{2+} , Mn^{2+}) and complexing agents (oxalic acid and EDTA) on the rate of the reaction is studied. The pseudo first order rate constants are computed graphically from **Log (absorbance) versus time** plot.

RESULTS AND DISCUSSION

Absorption spectra of the reaction mixture containing acetophenone oxime (1×10^{-2} M), chromium(VI) (2×10^{-3} M) and different concentrations (0.5 to 7.0 M) acetic acid are recorded immediately after mixing and also after a lapse of 12 hours. No significant change was noticed in the shape of the spectra with change in acid concentration. An inspection of the spectra reveals a decrease in the absorbance of chromium(VI) with time. No such decrease is however noticed if the reaction mixture does not contain the substrate (Fig. 1). This suggests that chromium(VI) is not undergoing any chemical reaction with the other components of the reaction mixture. Typical plot obtained between $-\text{Log}(\text{absorbance})$ vs time is shown in Fig. 2. A single straight line plot obtained indicates that the reaction is not complicated by side reactions. The rate constants computed from the linear plots obtained in different acid concentration are presented in Table 1. These results indicate that the rate change parallels the trend in acidity functions ($-\text{H}_0$).

Effect of Chromium(VI) Concentration

The effect of chromium(VI) concentration on the rate of the reaction at an optimum acid concentration (3.0 M) of acetic acid is studied and the results are presented in Table 2. The results show that the rate decreases

with increase of gross concentration of chromium(VI). This implies that the acid chromate ion (HCrO_4^-) is the effective oxidant since it is known¹ that its concentration decreases with increase of Cr(VI) concentration.

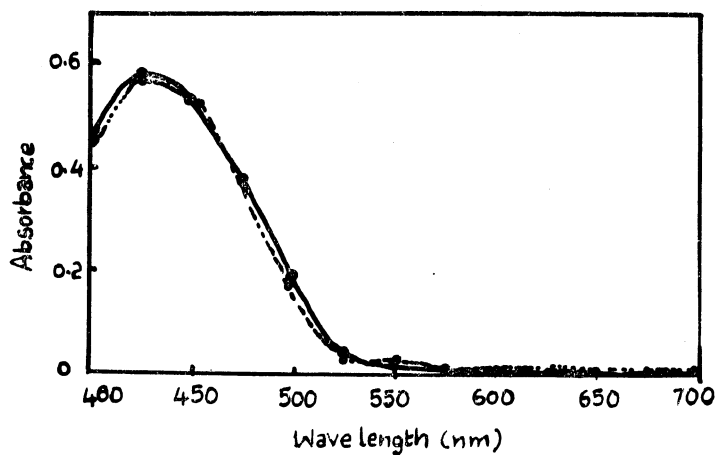


Fig. 1. A Absorbance vs wavelength
Absorption spectrum : [Chromium(VI)] = 2×10^{-3} M
Acetic acid = 3 M, DMF = 10%(v/v)

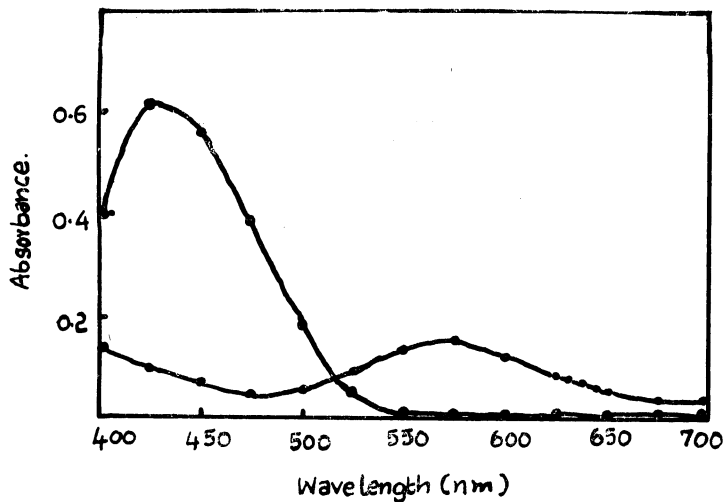


Fig. 1 B. Absorbance vs wavelength
Absorption spectrum : [Acetophenone oxime] = 1×10^{-2} M
[Chromium(VI)] = 2×10^{-3} , Acetic acid = 3 M, DMF = 10%(v/v)
(a) Immediate; (b) After 12 hours

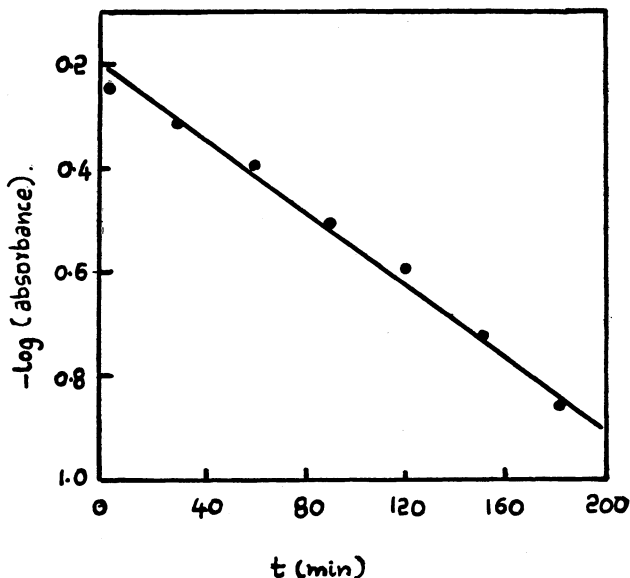


Fig. 2. Log(absorbance) versus time oxidative hydrolysis of acetophenone oxime (3 M acetic acid)

TABLE I
EFFECT OF ACETIC ACID CONCENTRATION
IN 10% (v/v) DMF AT 30°C

[APO] = 1×10^{-2} M; [Cr(VI)] = 2×10^{-3} M

[HoAc] (M)	$-H_0$	$10^4 K \text{ sec}^{-1}$
0.5	—	0.53
1.0	0.90	0.70
2.0	0.52	1.07
3.0	0.42	1.22
4.0	0.36	1.16
5.0	0.33	1.15
6.0	0.33	1.15
7.0	0.32	1.14

Effect of Oxime Concentration

The rate constant is measured in presence of different concentrations of the oxime keeping Cr(VI) and acetic acid concentrations at 2×10^{-3} M and 3 M respectively. The results are presented in Table 3.

TABLE 2
EFFECT OF CHROMIUM(VI) CONCENTRATION
IN 10%(v/v) DMF AT 30°C
[APO] = 1×10^{-2} M; [HoAc] = 3 M

[Chromium(VI)] (10^3 M)	10^4 K sec $^{-1}$
1.0	2.34
1.5	1.53
2.0	1.22
2.5	0.85

TABLE 3
EFFECT OF OXIME CONCENTRATION
IN 10%(v/v) DMF AT 30°C
[Cr(VI)] = 2×10^{-3} M; [HoAc] = 3M

[APO] 10^3 M	10^4 K sec $^{-1}$	K/[APO]
0.5	0.51	1.02
1.0	1.22	1.22
1.5	1.65	1.10
2.0	2.47	1.23
2.5	3.07	1.22
3.0	3.55	1.22

The rate constant (k) increase with the concentration of the oxime and shows first order dependence on the oxime concentration. $1/k$ versus $1/[\text{oxime}]$ gives a linear plot passing through the origin. This fact even-though is generally interpreted as that the prior complexation between chromium(VI) and oxime under the experimental conditions is absent, this does not always rule out the possibility of formation of transitory oxidant-substrate complex. It rather indicates that the formation constant of such an intermediate complex is very low.

Effect of Temperature

The activation parameters are evaluated by determining the rate of the reaction at 30, 35 and 40°C, keeping the concentration of chromium(VI), oxime and acid of 2×10^{-3} M, 1.0×10^{-2} M and 3.0 M respectively. The results are presented in Table 4. The magnitude of activation parameter suggests that the reaction is bimolecular.

TABLE 4
EFFECT OF TEMPERATURE ON THE RATE
OF ACTIVATION PARAMETERS
IN 10%(v/v) DMF
[HoAc] = 3.0 M; [APO] = 1×10^{-2} M;
[Cr(VI)] = 2×10^{-3} M

Temperature (°C)	10^4 K sec ⁻¹	ΔE^* KJ mole ⁻¹	$-\Delta S^*$ J deg ⁻¹ mole ⁻¹
30	1.22		
35	1.68	49.4	165.7
40	2.38		

Stoichiometry of the Reaction

The stoichiometry of the reaction is established as 1 : 1 (Chromium(VI) : Oxime) by determining the unreacted chromium(VI) spectrophotometrically in reaction mixture which contains large known excess of chromium (VI) and a known amount of oxime and which is kept for a large interval of time (> 12 hrs).

Effect of Solvent

The effect of dielectric constant on the rate is studied by determining the rate in different percentages (5 to 30% v/v) of dimethylformamide. It is ascertained from the spectra recorded that no change in the shape of the spectrum is produced by the increase of DMF content. The rate data is presented in Table 5. The rate decreases with dielectric constant implies

TABLE 5
EFFECT OF SOLVENT AT 30°C
[APO] = 1×10^{-2} M; [Cr(VI)] = 2×10^{-3} ; M[HoAc] = 3M

% DMF (v/v)	Dielectric constant	10^4 Ksec ⁻¹
5	74.0	1.54
10	73.0	1.22
15	72.0	0.85
20	71.0	0.69
25	70.0	0.51
30	68.4	0.35

that the reaction belongs to the type two molecules forming a polar product or two ions of the same sign.

Effect of Oxalic Acid

It is reported by Rocek *et al.*² that oxalic acid exhibits a rate benefit in chromic acid oxidations of the organic substrates. Hence the rate of the reaction is determined in presence of different concentrations (0.5×10^{-2} to 4.0×10^{-2} M) of oxalic acid. The results are presented in Table 6. It is seen from the data that the rate benefit is more in concentrations of oxalic acid greater than 3×10^{-2} M.

TABLE 6
EFFECT OF OXALIC ACID CONCENTRATION
IN 10% (v/v) DMF AT 30°C
[APO] = 1×10^{-2} M; [Cr(VI)] = 2×10^{-3} M; [HoAc] = 3M

[Oxalic acid] 10^2 M	10^4 Ksec ⁻¹
0.0	1.22
0.5	1.75
1.0	2.77
1.5	3.74
2.0	4.99
2.5	6.09
3.0	6.95
3.5	9.51
4.0	10.75

The order with respect to oxime is 0.7 in presence of oxalic acid in contrast to the first order in the absence of oxalic acid. It is also established by separate experiment that more chromium(VI) is consumed in presence of oxalic acid. This fact suggests that the reaction in presence of oxalic acid corresponds to a co-oxidation type rather than simple catalysis.

Effect of EDTA

Beek and Durham³ observed that the colour of the end product in the reduction of chromium(VI) by hydrazine in acid solutions is purple instead of the usual green colour in the presence of EDTA. The purple colour is shown to be due to Cr(III)-EDTA complex. But it is known that Cr(III) is extremely inert to substitution. Therefore some sort of complex must be envisaged with EDTA at least partially bound in the inner sphere of the chromium(VI). These authors have therefore studied the effect of

added EDTA on rate of chromium(VI)—hydrazine reaction. They report a monotonous increase in rate with increase of EDTA concentration. Venkatasubramaniam and co-workers⁴ observed an acceleration in aqueous medium with two definite peaks at EDTA : Cr(VI) equal to 1 : 2 and 1 : 1 respectively.

It is noticed in the present studies that the colour of the reaction mixture at the end of the reaction is purple in presence of EDTA, while it is light blue in the absence of it. This suggests that the chromium(III) is complexed with EDTA. It therefore suggests that EDTA is entering into the inner co-ordinate sphere of chromium(VI) as reported for chromium(VI)—hydrazine reactions. The effect of EDTA on the rate of reaction between chromium(VI) and the oxime is studied and the results are presented in Table 7.

TABLE 7
EFFECT OF EDTA CONCENTRATION IN
10% (v/v) DMF AT 30°C
[APO]= 1×10^{-2} M; [HoAc]=3.0 M;
[Cr(VI)]= 2×10^{-3} M

[EDTA] 10^3 M	$10^4 K \text{ sec}^{-1}$
0.4	1.28
1.2	1.28
2.0	1.28
4.0	1.05
6.0	0.91
8.0	0.85
10.0	0.78

It is observed that the rate remains constant till EDTA is equal to Cr(VI). The rate however decreases if [EDTA] is greater than [Cr(VI)]. Studied carried out in the absence of oxime under similar conditions revealed that reduction of Cr(VI) by EDTA is extremely slow in acetic acid medium. The order with respect to oxime is 0.7 in presence of EDTA.

The fractional order in the presence of oxalic acid or EDTA indicates that the substrate is involved in complex formation with chromium(VI) or the added compound (oxalic acid or EDTA). In the concentration ranges of the substrates used in the present study, there is no positive evidence of complex formation between the oxidant and the oxime either from kinetic or spectrophotometric data. Complex formation between

oxime and oxalic acid or EDTA is also not expected. Therefore it is probable that a ternary complex between chromium(VI), oxime and EDTA or oxalic acid is formed. It is further noticed that the order with respect to oxalic acid is one. The rate laws under the experimental conditions thus come out to be

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{k K[\text{oxalic acid}][\text{oxime}][\text{HCrO}_4^-]}{1 + k[\text{oxime}]}$$

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{k K[\text{oxime}][\text{HCrO}_4^-]}{1 + k[\text{EDTA}] + k[\text{oxime}]}$$

Substituent Effect

It is known that in chromic acid oxidation of organic substrates, the substrate loses a hydrogen atom as (1) a proton or (2) a hydride ion or (3) hydrogen atom. The one or the other of the above possibilities is usually ascertained through the substituent influence on the rate. A positive value for reaction constant (ρ) suggests that the removal of hydrogen is a proton. A negative ρ value is expected if the hydrogen is lost as an hydrogen atom resulting in the formation of a free radical of the substrate. A ρ value ranging between 0.5 and 1.5 was reported for radical reactions⁵⁻⁹. The rate studies are therefore carried out on the *para* substituted acetophenone oximes and the results are presented in Table 8.

TABLE 8
EFFECT OF SUBSTITUENT IN 10% (v/v)
DMF AT 30°C
[Oxime] = 1×10^{-2} M; [Cr(VI)] = 2×10^{-3} M;
[HoAc] = 3.0 M

Substituent	σ	10^4 K sec^{-1}
p-NO ₂	+0.78	0.21
p-Cl	+0.23	0.73
H	0.00	1.22
p-CH ₃	-0.17	1.36
p-OCH ₃	-0.27	1.55
p-OH	-0.37	0.62
p-NH ₂	-0.66	1.00

It is seen from the results that the rate increases as the electron donating nature of the substituent increases. The plot between log k and σ gave a straight line with a slope of -0.80 . The negative value of ρ thus indicates that the hydrogen atom is lost as an hydrogen atom and the

mechanism corresponds to a radical mechanism. This fact is further substantiated by the initiation of the polymerisation of acrylonitrile by Cr(VI) + oxime system. The reports made in the literature on the oxidation of oximes of Tl(III)¹⁰, Mn(III)¹¹, Ce(IV) and Pb(IV)¹² indicate the formation of an iminoxy radical. It is seen from the log k - σ plot that *para* amino and *para* hydroxy acetophenones show greater deviation. This suggests that resonance effects are more significant in these compounds. The rate with the substrates is much less than what is expected. This implies that the free radical of these substrates is established under the experimental conditions.

Activation Parameters

To have more clear insight into the mechanism, studies are carried out at three different temperatures (30, 35 and 40°C) and the activation parameters are calculated. These are presented in Table 9. The results

TABLE 9
ACTIVATION PARAMETERS FOR THE OXIDATIVE HYDROLYSIS OF ACETOPHENONE OXIME AND SUBSTITUTED OXIMES
IN 10% (v/v) DMF AT 30°C

[Oxime] = 1×10^{-2} M; [Cr(VI)] = 2×10^{-3} M;
[HoAc] = 3.0 M

Substituent	10^4 K sec ⁻¹	ΔE^* ΔH^* ΔG^*			$-\Delta S^*$
		KJ mole ⁻¹			
p-NO ₂	0.21	49.8	52.3	106.3	179.5
p-Cl	0.73	46.0	47.5	102.9	180.7
H	1.22	49.4	51.9	102.9	165.7
p-CH ₃	1.36	44.4	46.9	102.5	182.0
p-OCH ₃	1.55	37.7	40.2	103.8	202.9
p-OH	0.62	59.8	62.3	101.6	130.0
p-NH ₂	1.00	36.4	38.9	97.5	191.3

show that the activation energy changed with change of structure. But ΔG^* for the oximes is the same. This constancy in ΔG^* may be explained on the basis of isokinetic relationship¹³ implying that the same mechanism operates. The plot of ΔH^* versus ΔS^* was linear with a slope equal 300°K (isokinetic temperature). The nearness of the experimental temperature (303°K) to the isokinetic temperature is probably the reason for the small substituent effect observed.

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CORRIGENDUM

Paper entitled "5-Methyl-s-triazolo (3,4-*b*) benzothiazole as an antioxidant for mustard oil stability" [*Asian J. Chem.*, Vol. 4, No. 2, 397-399 (1992)]

In the title of this paper please substitute 5-Methyl instead of 5-Metal.