Asian Journal of Chemistry Vol. 11, No. 4 (1999), 1397–1401

Kinetics of the Oxidation of Ethyl Acetate by Potassium Dichromate

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Potassium dichromate exists as an important oxidising agent. In this paper, we report the kinetics of oxidation of ethyl acetate by potassium dichromate in acid-water and solvent-water mixtures at different temperatures. Also we have reported the dependence of rates of reaction on concentration of oxidant and substrate.

INTRODUCTION

Potassium dichromate is reported as a powerful and versatile oxidant. A number of reports are available on oxidation with Cr(VI) oxidant.[1–3] In the oxidation of esters by a series of oxidants like Ce(IV), Co(III), Mn(VII), Mn(III), Ti(III) and $S_2O_8^{2-}$, an attempt was made to find whether the ester is (i) directly oxidised or (ii) undergoes hydrolysis prior to oxidation.[4–6] No conclusive evidence has been provided by earlier workers in support of either of the two pathways (i or ii), in the oxidation of esters by Cr(VI). Hence, it was thought worth while to study the kinetics of oxidation of ethyl acetate by Cr(VI). The oxidation of ethyl acetate is a very important kind of chemical reaction. The effect of introducing solvent in the reaction system has also been studied.

EXPERIMENTAL

All the chemicals used were of analytical grade. Double distilled water was used. Ethyl acetate (Sisco Chemicals) was purified before use. Potassium dichromate, perchloric acid, acetic acid and acetone were used of E. Merck.

The experiments were carried out spectrophotometrically using Bausch and Lomb Spectronic-20 at different temperatures. The reaction rates were studied by following the absorbance decrease at 350 nm corresponding to a Cr(VI) absorption maximum as a function of time and was found to obey Beer's law.

RESULTS AND DISCUSSION

[A] oxidation of ethyl acetate by Cr(VI) in perchloric acid medium at different temperatures is shown in Table 1(a).

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TABLE-1(a)
PSEUDO FIRST ORDER RATE CONSTANTS FOR THE OXIDATION OF ETHYL ACETATE BY Cr(VI) IN AQUEOUS PHASE AT DIFFERENT TEMPERATURES.
[Ethyl Acetate] = 0.1 M, $[HClO_4]$ = 1.5 M, $[K_2Cr_2O_7] = 4 \times 10^{-4}$ M

Temperatures (°C)	$10^2 \times K_{obs}$ min^{-1} Ethyl acetate
30	1.9191
35	2.2015
40	2.5810

[B] Oxidation of ethyl acetate by Cr(IV) at different perchloric acid concentrations in aqueous phase at 30°C is tabulated in Table 1(b).

TABLE-1(b)
PSEUDO FIRST ORDER RATE CONSTANTS FOR THE OXIDATION OF ETHYL ACETATE BY Cr(VI) IN AQUEOUS PHASE AT DIFFERENT PERCHLORIC ACID CONCENTRATIONS AT 30°C.
[Ethyl Acetate] = 0.1 M, $[K_2Cr_2O_7] = 4 \times 10^{-4}$ M

$[HClO_4]$ M	$10^2 \times K_{obs}$ min^{-1} Ethyl acetate
0.75	0.8225
1.00	1.2150
1.25	1.5603
1.50	1.9191

The increase in the temperature tended to pronouncedly increase the oxidation of ethyl acetate. Also there is an increase in the rate with increase in the concentration of perchloric acid. The plot of rate constants versus $[H^+]$ is found to be linear passing through origin indicating the reaction of first order.

[C] The plot of pseudo first order rate constants for oxidation of ethyl acetate at different concentrations of ethyl acetate in perchloric acid medium is shown in Fig 1(a). This plot of rate constants (K) versus [ethyl acetate] was found to be linear passing through origin indicating the reaction to be of first order.

[D] Oxidation of ethyl acetate by Cr(VI) in perchloric acid medium at different acetic acid-water mixtures at 30°C has been studied to find the nature of Cr(VI) species participating in the reaction. The rate of oxidation is found to increase with increase in acetic acid content. Table 1(c).

The plot of volume % of acetic acid versus rate K is found to be linear. The plot of mole fraction of acetic acid-water composition versus log K is also found to be linear. Also the variation of logarithms of the pseudo first order rate constants for the oxidation of ethyl acetate with $1/\varepsilon$ is shown in Fig. 1(b), where ε is the dielectric constant of the medium. The values of dielectric constant at the acid-water compositions and temperature of study are interpolated from the value

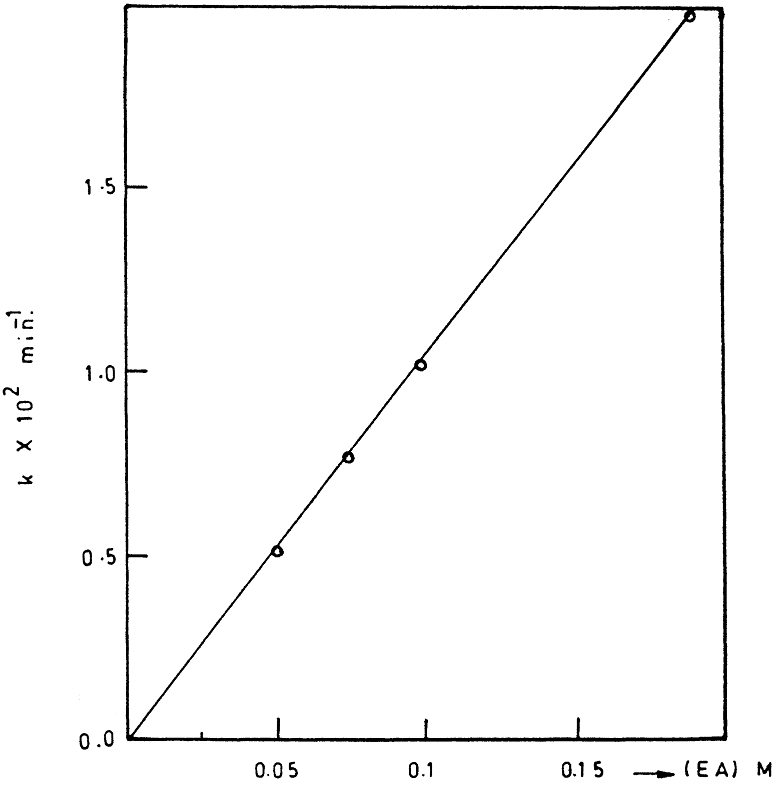


Fig. 1(a) Dependence of rate constants on the ester concentrations in the oxidation of ethyl acetate by Cr(VI) at 30°C

of Alkerlof[7]. For acetic acid-water mixture, log K varied linearly with 1/ε having a positive slope as per predictions of equation of Laidler and Eyring[8], Amis and Jaffe[9]. It is well known according to Amis[10], that the reactions which go rapidly with decrease in dielectric constant are all positive ion-dipole reactions. The positive species may be $HCrO_3^+$ or $H_3CrO_4^+$ which was shown to be a reactive species in the oxidation of aliphatic esters and benzoin.

TABLE-1(c)

RATES FOR THE OXIDATION OF ETHYL ACETATE BY Cr(VI) IN PERCHLORIC ACID MEDIUM AT DIFFERENT ACETIC ACID-WATER MIXTURES AT 30°C

[Ethyl Acetate] = 0.1 M, $[HClO_4]$ = 0.75 M, $[K_2Cr_2O_7] = 4 \times 10^{-4}$ M

Volume (%) (CH_3COOH/H_2O)	Dielectric constant (ε)	1/ε	$10^2 \times K_{obs}$ min^{-1} Ethyl acetate
0	–	–	0.8225
10	75.83	0.01318	1.6832
20	72.95	0.01370	2.7794
30	69.72	0.01434	3.7662
40	65.80	0.01519	4.8110
50	61.04	0.01638	5.3476

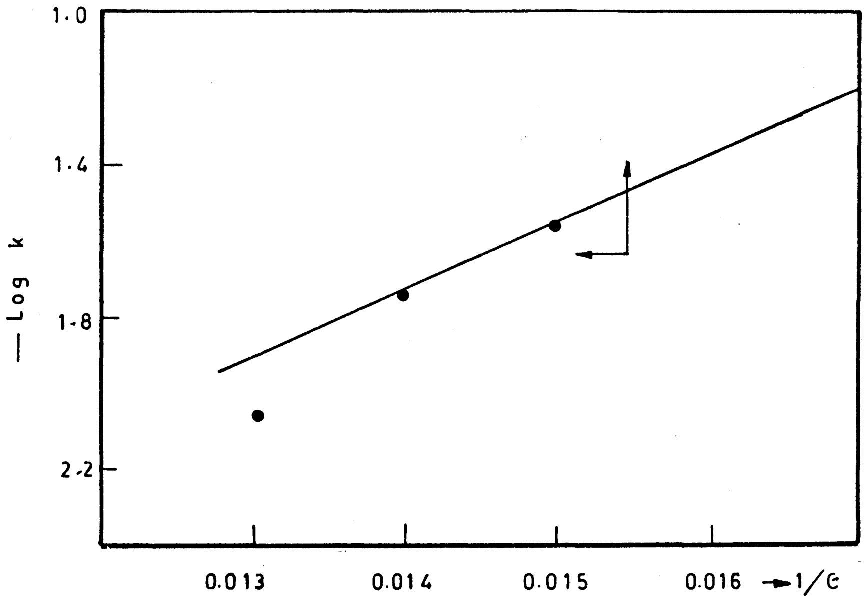
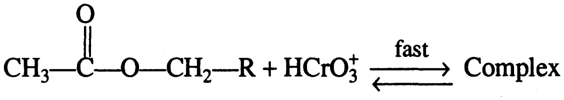


Fig. 1(b) Plot of dielectric constant (1/ε) of acetic acid-water mixture versus –log. k at 30°C for ethyl acetate.

The following mechanism consistent with the above results has been proposed for oxidation of esters by Cr(VI) in perchloric acid medium in aqueous phase and in acetic acid medium.



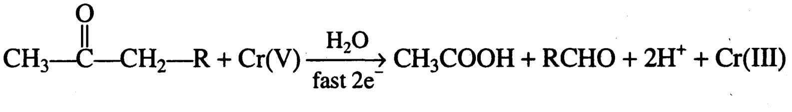
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-R + HCrO_3^+ \underset{\longleftarrow}{\xrightarrow{\text{fast}}} \text{Complex} \quad (1)$$

$$\overset{K''}{\text{Complex}} \xrightarrow{\text{Slow}} CH_3COOH + RCHO + Cr(IV) \quad (2)$$

$$Cr(IV) + Cr(VI) \xrightarrow{\text{fast}} 2Cr(V) \quad (3)$$

or

$$2Cr(IV) \xrightarrow{\text{fast}} Cr(V) + Cr(III) \quad (4)$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-R + Cr(V) \xrightarrow[\text{fast } 2e^-]{H_2O} CH_3COOH + RCHO + 2H^+ + Cr(III)$$

[E] Oxidation of ethyl acetate by Cr(VI) in perchloric acid medium at different acetone-water mixtures at 30°C have been studied. This is tabulated in Table 1(d).

TABLE-1(d)
RATES FOR THE OXIDATION OF ETHYL ACETATE BY Cr(VI) IN PERCHLORIC ACID MEDIUM AT DIFFERENT ACETONE-WATER MIXTURES AT 30°C
[Ethyl acetate] = 0.1 M, $[HClO_4] = 0.75$ M, $[K_2Cr_2O_7] = 4 \times 10^{-4}$ M

Volume (%) (CH_3COOH/H_2O)	Dielectric constant (ε)	1/ε	$10^2 \times K_{obs}$ min^{-1} Ethyl acetate
0	–	–	0.8225
10	76.75	0.01302	1.4896
20	74.96	0.01334	2.2594
30	72.82	0.01373	2.9052
40	70.22	0.01424	3.3979
50	67.87	0.01473	4.2882

The plot of volume % of acetone versus rate K is found to be linear.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. K.R. Desai, Head, Chemistry Department, South Gujarat University, Surat. The author Homi Z. Guard expresses thanks to the Principal, Dr. J.C. Vyas, and Dr. G.N. Mehta, Head of Applied Sciences and Humanity Department of S.V. Regional College of Engg. and Technology, Surat-395 007, India for providing research facilities, helpful suggestions and cooperation.

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(*Received*: 26 April, 1999; *Accepted*: 24 July 1999) AJC-1804