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Influence of Amides and Salts on the Oxidation of Methyl Acetate and Ethyl Acetate by Potassium Dichromate

H.Z. GUARD*, D.M. KOTHWALA, D.R. JOSHI and T.N. NAGAR†
Department of Chemistry, South Gujarat University
Surat-395 007, India

In this paper, we are reporting the kinetics of oxidation of methyl acetate and ethyl acetate by potassium dichromate in acid-water and solvent-water mixtures using amides, salts and surfactants.

INTRODUCTION

There has been a continued interest in the development of methyl acetate and ethyl acetate as an important substrate[1]. Cr(VI) exists as an effective and selective oxidant for organic substrate under different reaction conditions[2, 3]. In this paper we have studied the oxidation of methyl acetate and ethyl acetate with Cr(VI) in presence of salts, amides and surfactants.

EXPERIMENTAL

All the chemicals used were of high degree of purity: methyl acetate, ethyl acetate (Sisco Chemicals); potassium dichromate, perchloric acid, acetone, acetic acid (E. Merck); sodium dodecyl sulphate, sodium sulphate, chromium sulphate, aluminium sulphate, manganous sulphate (BDH); urea, sodium chloride, acetamide (Poly Pharm); double distilled water was used.

The kinetic measurements were carried out spectrophotometrically using Bausch and Lomb Spectronic-20. 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] Influence of amides on oxidation of methyl acetate and ethyl acetate by Cr(VI) in perchloric acid medium

Urea and acetamide strongly retarded the oxidation of *n*-butyl acetate by Cr(VI). The decrease in oxidation of these esters were found to be more in urea than acetamide. The rate constants decrease exponentially with increase in concentration of urea.

The bonding of H^+ ions with the oxygen of amides (C=O) in retarding the rate is much more as compared to the effect of the increased dielectric constant of the medium in increasing the rate. The retardation of rate in presence of urea

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*Department of Chemistry, SVR College of Engg. and Tech., Surat-7, India.

may be by keeping the H^+ ions by forming a complex and the potential binding centre is the oxygen of >C=O group[4]. Effect of additives on pseudo first order rate constants for oxidation of methyl acetate and ethyl acetate by Cr(VI) at 30°C are tabulated in Table-1.

TABLE-1
EFFECT OF ADDITIVES ON PSEUDO FIRST-ORDER RATE CONSTANTS FOR OXIDATION OF METHYL ACETATE AND ETHYL ACETATE BY Cr(VI) AT 30°C.

[esters] = 0.1 M, $[HClO_4]$ = 1.5 M, $[K_2Cr_2O_7] = 4 \times 10^{-4}$ M

	$10^2 \times K_{obs}$ min^{-1}						
Additives M	0.00	0.25	0.50	1.0	1.5	2.0	2.5
Methyl acetate							
K (Urea)	1.1810	0.5380	0.3280	0.2441	0.2005	0.1994	0.1876
K (NaCl)	1.1810	0.4797	0.3108	0.2208	0.1831	0.1609	0.1392
K (Acetamide)	1.1810	0.7215	0.5280	0.3979	0.2712	0.2240	0.2012
K (NaCl + 1 M urea)	0.2441	0.0953	0.0894	0.0723	0.0675	–	–
Ethyl acetate							
K (Urea)	1.9191	1.8323	1.7440	1.2305	0.7818	0.5702	0.4406
K (NaCl)	1.9191	0.5918	0.4797	0.3927	0.3152	0.2613	0.1942
K (Acetamide)	1.9191	1.8721	1.8500	1.5660	1.3895	1.2000	1.1200
K (NaCl + 1 M urea)	1.2305	0.3725	0.3165	0.2453	0.1825	0.1213	0.0931

[B] Effect of urea on the oxidation of methyl acetate and ethyl acetate by Cr(VI) in presence of anionic surfactant, sodium dodecyl sulphate (SDS) with pseudo first-order rate constant values

These are presented in Table-2.

TABLE-2
EFFECT OF UREA IN PRESENCE OF SDS ON PSEUDO FIRST-ORDER RATE CONSTANTS FOR OXIDATION OF METHYL ACETATE AND ETHYL ACETATE BY Cr(VI) IN PERCHLORIC ACID MEDIUM AT 30°C TEMPERATURE

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

	$10^2 \times K_{obs}$ min^{-1}				
Additives M	0.00	0.25	0.50	0.75	1.00
Methyl acetate					
K(Urea)	0.5757	0.4245	0.3698	0.3413	0.3173
K(0.12 M SDS)	1.2728	1.0070	0.8397	0.7852	0.7285
Ethyl acetate					
K(Urea)	0.8225	0.5456	0.3958	0.3453	0.3266
K(0.12 M SDS)	1.4652	1.0070	0.7676	0.6841	0.6280

In the combined environment of urea and SDS micelles it is found that urea shows a normal retarding effect on the rate constant due to its association with H^+ ions and destroying the micelles. Urea hinders the association of hydrophobes because of its demicellisation properties[5, 6].

[C] Effect of salts on oxidation of methyl acetate and ethyl acetate by Cr(VI) in perchloric acid medium and 20% (v/v) acetic acid-water mixture.

The rate constant in 20% (v/v) acetic acid-water mixture for ethyl acetate in presence of added salts, *viz.*, $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$, $MnSO_4$ and Na_2SO_4 are tabulated in Table 3 and 4. It is found that these salts decreased the rate constant of the reaction.

TABLE-3
EFFECT OF VARYING SALTS ON THE OXIDATION OF ETHYL ACETATE BY Cr(VI) IN 0.75 M $HClO_4$ AND 20% (v/v) ACETIC ACID-WATER MIXTURE AT 30°C
[ethyl acetate] = 0.1 M, $[K_2Cr_2O_7] = 4 \times 10^{-4}$ M

[Salts] M	$10^2 \times K_{obs}$ min^{-1}	
	$Cr_2(SO_4)_3$	$Al_2(SO_4)_3$
0.0000	2.7794	2.7794
0.0005	1.6400	1.8800
0.0010	1.1600	1.5800
0.0050	0.7509	1.1594
0.0100	0.6022	0.9238

TABLE-4
EFFECT OF VARYING SALTS ON THE OXIDATION OF ETHYL ACETATE BY Cr(VI) IN 0.75 M $HClO_4$ AND 20% (v/v) ACETIC ACID-WATER MIXTURE AT 30°C
[ethyl acetate] = 0.1 M, $[K_2Cr_2O_7] = 4 \times 10^{-4}$ M

[Salts] M	$10^2 \times K_{obs}$ min^{-1}	
	Na_2SO_4	$MnSO_4$
0.000	2.7794	2.7794
0.001	1.6400	1.6121
0.025	1.4969	1.1500
0.075	0.9127	1.0660
0.120	0.7723	0.7980
0.200	0.6576	0.7617

The rate of retardation (K_{obs}/K_O) for methyl acetate in presence of this salts in 20% acetic acid-water mixture are shown in Fig. 1 (a) and (b).

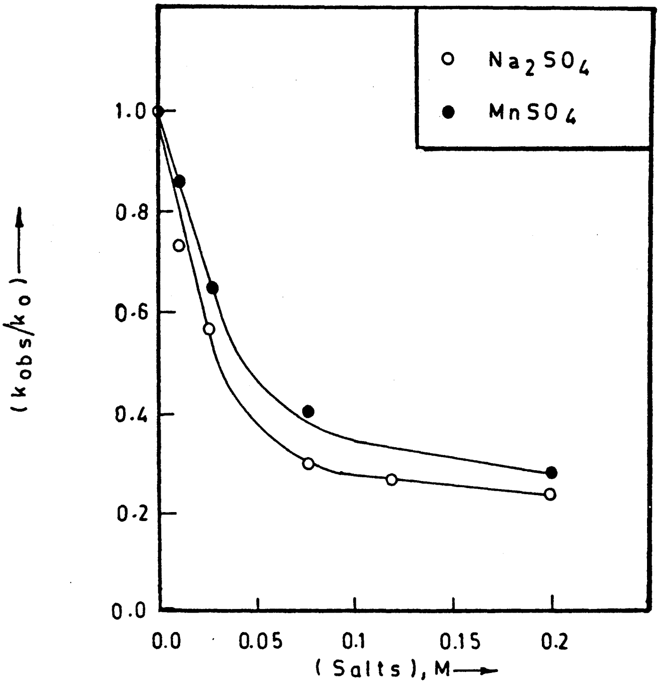

Fig. 1(a) Dependence of (k_{obs}/k_o) on salts concentrations for the oxidation of methyl acetate by Cr(VI) in 20% (v/v) acetic acid-water mixture at 30°C.

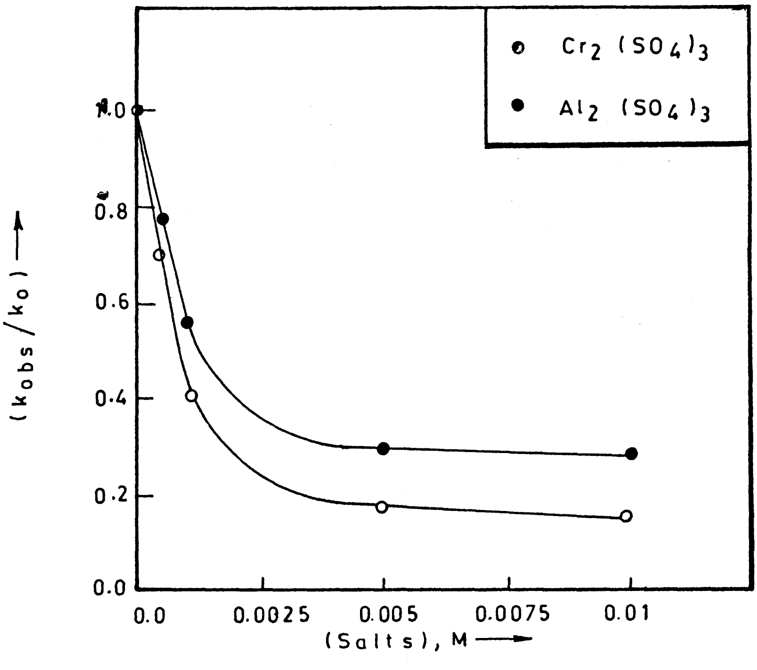

Fig. 1(b) Dependence of (k_{obs}/k_o) on salts concentrations for the oxidation of methyl acetate by Cr(VI) in 20% (v/v) acetic acid-water mixture at 30°C.

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