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Kinetics and Mechanism of Oxidation of Dimethyl Malonate and Diethyl Malonate by Chromic Acid in the Presence and Absence of Oxalic Acid in Acetic Acid-Water Medium

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The kinetics of oxidation of esters by chromic acid has been investigated in acetic acid-water mixtures in the presence and absence of oxalic acid. In the absence of oxalic acid, the reaction is overall second order, first order in each reactant. The reaction rates are independent of the added salts, while in the presence of oxalic acid the rate of oxidation increases. The products are identified and activation parameters have been calculated.

Key Words: Kinetics, Chromic acid, Dimethyl malonate, Diethyl malonate, Oxalic acid.

INTRODUCTION

The oxidation of esters by a series of oxidants like Ce(IV)[1], Co(III)[2], Mn(VII)[3], Mn(III)[4], Ti(III)[5], vanadium(V)[6] and $S_2O_8^{2-}$,[7] several attempts were made to find out whether the ester is directly oxidized or it undergeos hydrolysis prior to oxidation. So far no conclusive evidence was given in support of either of the two pathways in oxidation of esters by earlier workers[8]. The work was carried out in the presence and absence of oxalic acid to understand the mechanism.

EXPERIMENTAL

All the chemicals used were of AR grade. Chromic acid was prepared from potasium dichromate. Double distilled water was used to prepare stock solutions. The course of the reaction was studied spectrophotometrically using Coronation Digital Colorimeter 063 model.

RESULTS AND DISCUSSION

Oxidation of esters in absence of oxalic acid

[Ester] $\gg$ [Cr(VI)] *vs.* time, the plot of log Cr(VI) is linear indicating the order in [Cr(VI)] to be unity (Fig. 1).

From the slopes of the pseudo-first order, rate constant have been calculated for different esters at different concentrations (Table-1).

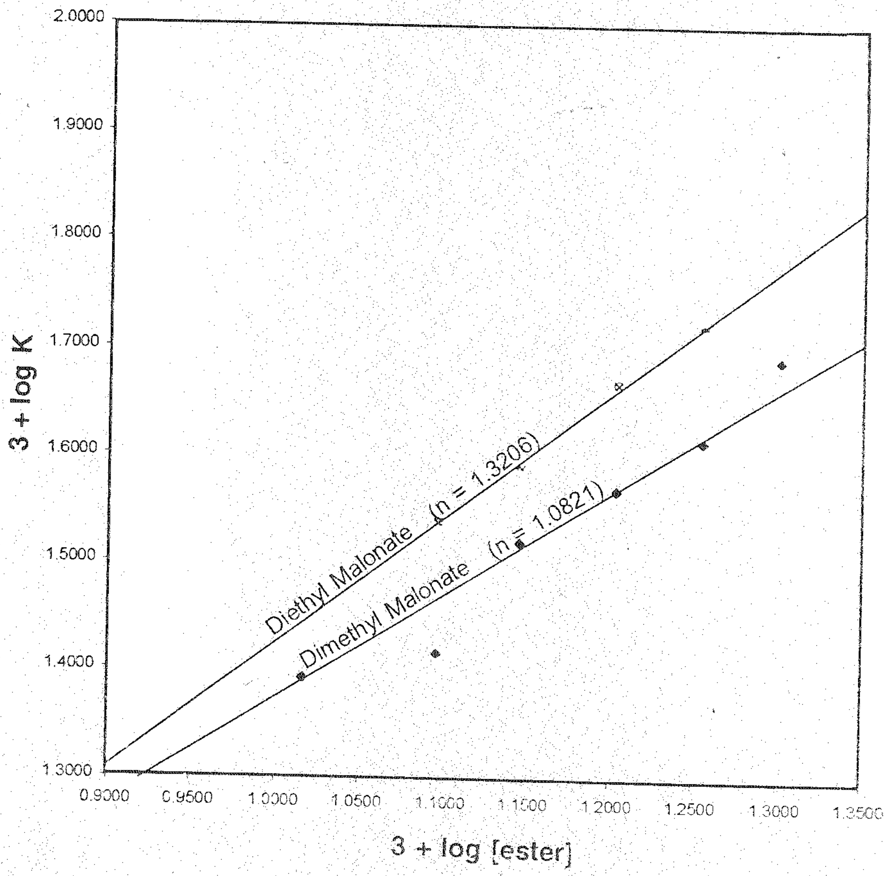


Fig. 1. Effect of varying [ester] on oxidation of dimethyl malonate and diethyl malonate ([Cr(VI)] = 5 × 10^{-3} M, [HOAc] = 20% (v/v), H_2SO_4 = 3.0 M, Temp. = 35°C ± 0.01°C)

TABLE-1

EFFECT OF VARYING SUBSTRATE ON THE RATE OF OXIDATION OF DIMETHYL MALONATE AND DIETHYL MALONATE

[Cr(VI)] = 5 × 10^{-3} M, [HOAc] = 20% (v/v), H_2SO_4 = 3.0 M, Temp. = 35°C ± 0.01°C

[ester] (M)	3 + log [ester]	Dimethyl malonate		Diethyl malonate	
		K × 10^{-2}	3 + log K	K × 10^{-2}	3 + log K
0.0200	1.3010	4.917	1.6917	7.724	1.8878
0.0180	1.2553	4.111	1.6139	5.261	1.7211
0.0160	1.2041	3.710	1.5694	4.455	1.6679
0.0140	1.1461	3.307	1.5194	3.881	1.5889
0.0125	1.0969	2.607	1.4161	3.461	1.5392
0.0104	1.0170	2.464	1.3916	3.060	1.4857

Effect of variation of [H_2SO_4]

The rate of oxidation of esters increases with increase in concentration of sulphuric acid under the conditions:

[Cr(VI)] = 5×10^{-3} M, [HOAc] = 20% (v/v), [ester] = 5×10^{-2} M, temperature = 308 K, $\mu = 0.1$ M

The pseudo first order rate constant of oxidation of dimethyl malonate increases from 1.750×10^{-2} to 7.5040×10^{-2} min^{-1} and for diethyl malonate 2.888×10^{-2} to 13.12×10^{-2} min^{-1}.

The reaction rate is not affected by the addition of SO_4^{2-} ions and the H^+ ions are responsible for the increase in rate constant.

Effect of variation of solvent

The effect of solvent (acetic acid) has been studied from 20–50%. The rate of reaction increases with the increase in concentration of acetic acid (Table-2).

The plot of log K *vs.* 1/D is linear with a +ve slope (Fig. 2) indicating that the reaction is positive ion dipole type[9]. Hence, the attacking species is said to be $HCrO_3^+$, which is also reactive species in the oxidation of benzoin[10].

TABLE-2
EFFECT OF VARYING CONCENTRATION OF ACETIC ACID ON THE OXIDATION OF DIMETHYL MALONATE AND DIETHYL MALONATE

[Cr(VI)] = 5×10^{-3} M, [H_2SO_4] = 3.0 M, [ester] = 5×10^{-2} M, Temp. = 35 ± 0.01°C

[HOAc] (%) (v/v)	1/D × 10^3 K^{-1}	Dimethyl malonate		Diethyl malonate	
		K × 10^{-2} min^{-1}	log K	K × 10^{-2} min^{-1}	log K
20	15.15	2.015	–1.6957	1.648	–1.7830
25	17.85	2.252	–1.6474	2.190	–1.6596
30	19.05	2.662	–1.5748	2.321	–1.6343
35	20.29	2.873	–1.5417	2.527	–1.5974
40	21.74	3.091	–1.5099	2.828	–1.5485
45	23.50	3.563	–1.4482	3.464	–1.4604
50	25.24	4.068	–1.3906	4.889	–1.3108

Effect of varying temperature on the rate constant

The rate constant increases with increase in temperature. The activation energies have been calculated from the slopes of Arrhenius plots, in the temperature range 20–45°C.

The products of oxidation are identified as acetic acid and corresponding aldehydes. The rate data for the oxidation of diethyl malonate by Cr(VI) in sulphuric acid are presented in Table-3 along with the activation parameters.

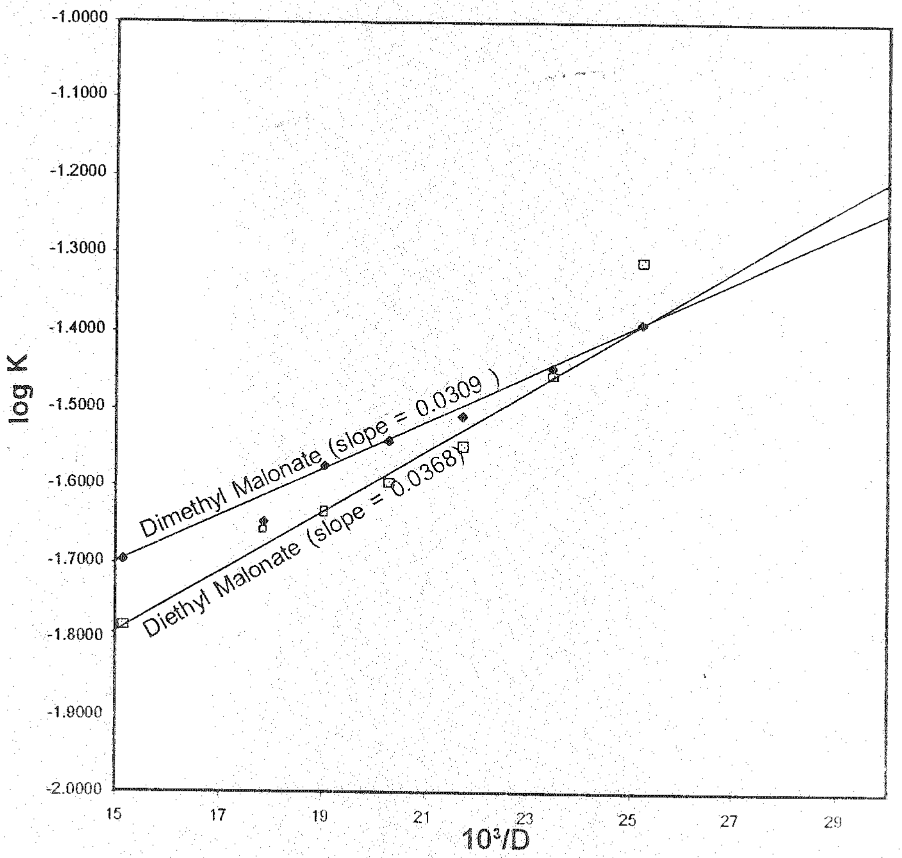


Fig. 2. Effect of varying solvent composition ([Cr(VI)] = 5×10^{-3} M, [H_2SO_4] = 3.0 M, [ester] = 5×10^{-2} M, Temp. = 35 ± 0.01°C)

TABLE-3

T°K	1/T × 10^3 M	K × 10^{-2} min^{-1}	log K	$\Delta H^{\#}$ = 2.303 × Slope R	$\Delta H^{\#}$ = E − R × T	$\Delta S^{\#}$	$\Delta G^{\#}$	A = log^1 (log A)
				Dimethyl malonate				
308	3.2468	2.568	−3.3686	6744.6563	6132.66	−54.1096	22798.4216	2.612E + 01
				Diethyl malonate				
308	3.2468	2.833	−3.3259	7225.1427	6613.15	−52.3544	2278.3082	6.316E + 01

The reactions are characterized by the –ve value of entropy of activation. It suggests that the rate of disappearance of esters is slower and the activation complex is less probable (Fig. 3).

The negative entropies of activation have been found for outer sphere, electron transfer reactions between ions of like charges.

The redistribution of energy along various degrees of freedom in the formation of activated complex suggests a complex molecule formation as shown in the reaction steps.

It was found that the reactivity of diethyl malonate is greater than dimethyl malonate due to increasing polar effect of alkyl group in dimethyl malonate.

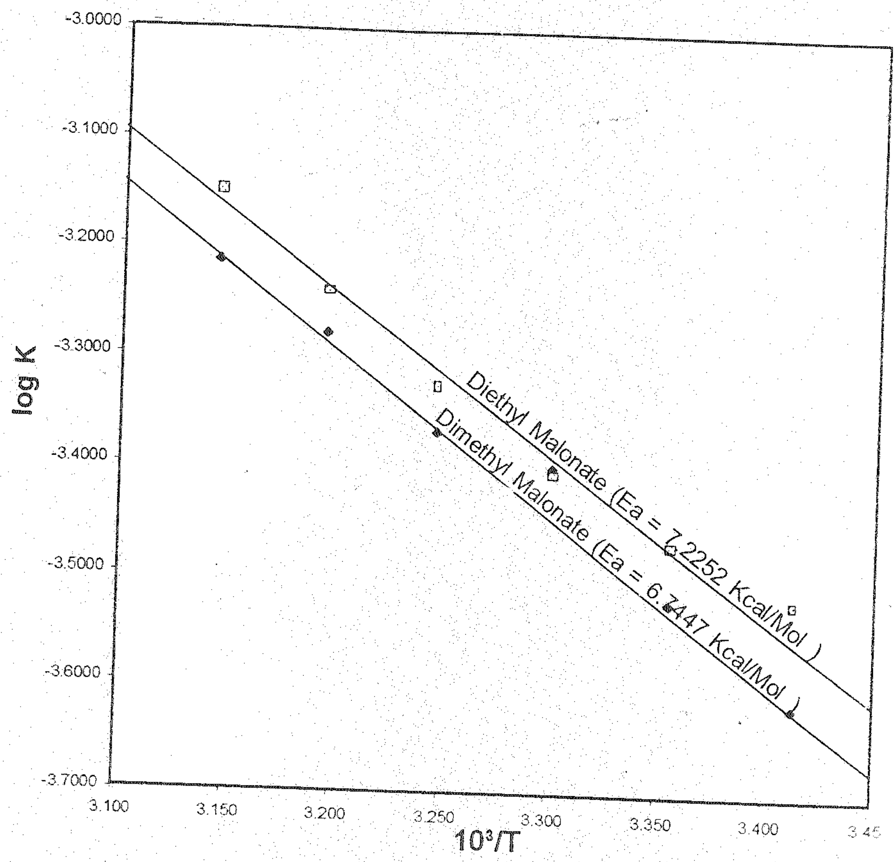
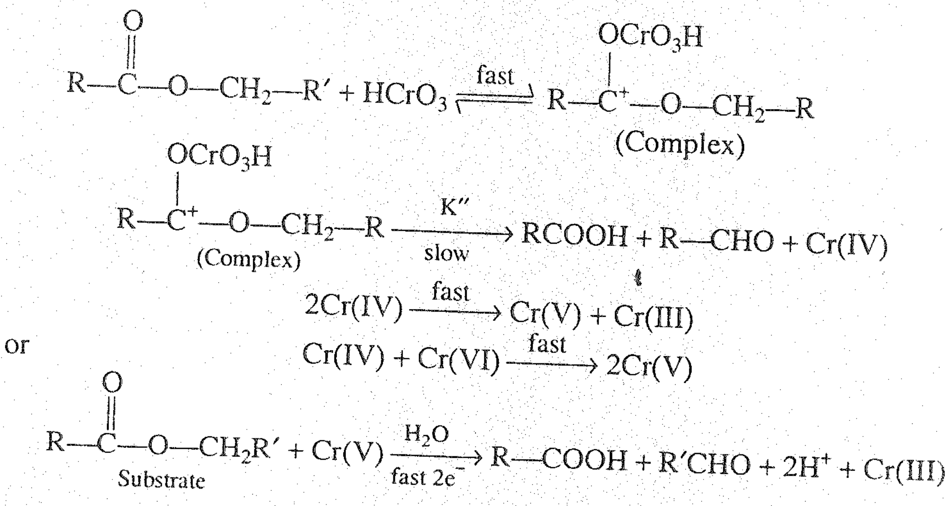


Fig. 3. Effect of varying temperature ([Cr(VI)] = 5×10^{-3} M, [H_2SO_4] = 3.0 M [ester] = 5×10^{-2} M, [HOAC] = 20% (v/v)

Oxidation mechanism of esters in absence of oxalic acid

The present work has been carried in 20% (v/v) acetic acid-water mixtures in presence of 3.0 M H_2SO_4. Under similar conditions the hydrolysis rate constant of diethyl malonate by Cr(VI) is found to be 2.7×10^{-5} min^{-1} which is several times lower than the rate of oxidation of esters by Cr(VI) hence can be considered as negligible **(Scheme-1)**.



$$R-\overset{\overset{O}{\|}}{C}-O-CH_2-R' + HCrO_3 \overset{fast}{\rightleftharpoons} \underset{\text{(Complex)}}{R-\overset{\overset{OCrO_3H}{|}}{C^+}-O-CH_2-R} \quad (1)$$

$$\underset{\text{(Complex)}}{R-\overset{\overset{OCrO_3H}{|}}{C^+}-O-CH_2-R} \xrightarrow[slow]{K''} RCOOH + R-CHO + Cr(IV) \quad (2)$$

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

or

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

$$\underset{\text{Substrate}}{R-\overset{\overset{O}{\|}}{C}-O-CH_2R'} + Cr(V) \xrightarrow[fast\ 2e^-]{H_2O} R-COOH + R'CHO + 2H^+ + Cr(III) \quad (5)$$

Scheme-1

Oxidation of esters in presence of oxalic acid

The rate of reaction is much greater when oxalic acid and ester are present together than when either of the two substrates is taken separately.

The oxidation of ester alone by Cr(VI) is first order in [diethyl malonate] and [dimethyl malonate]. However, in presence of oxalic acid the order in [ester] is fractional (Table-4, Fig. 4).

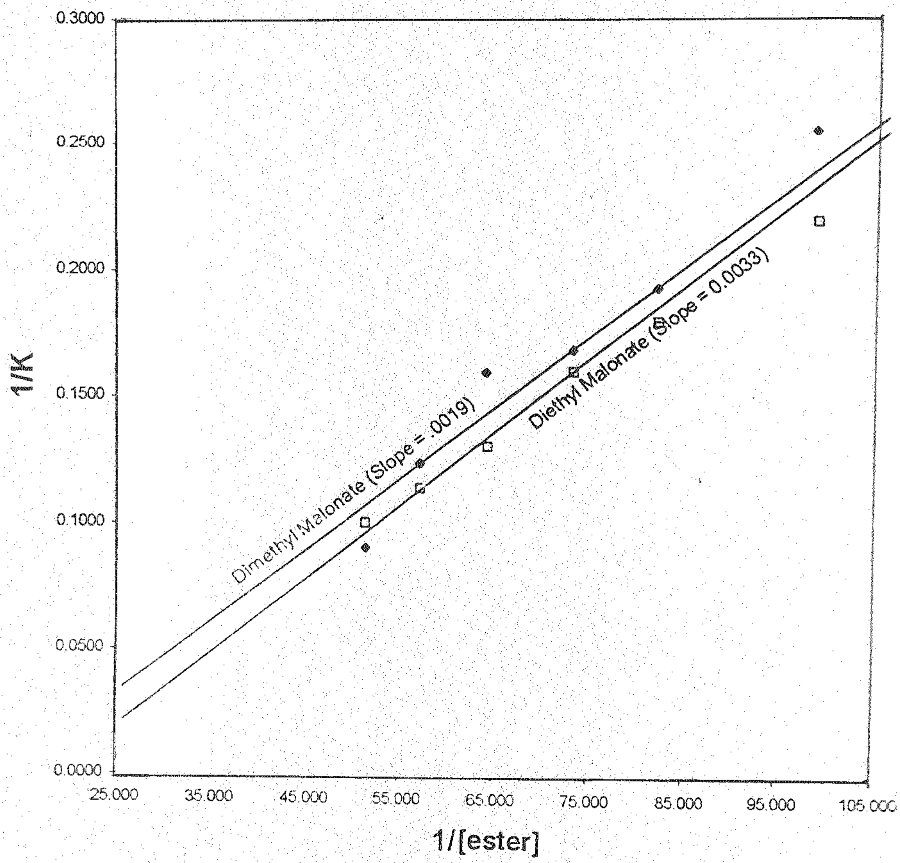


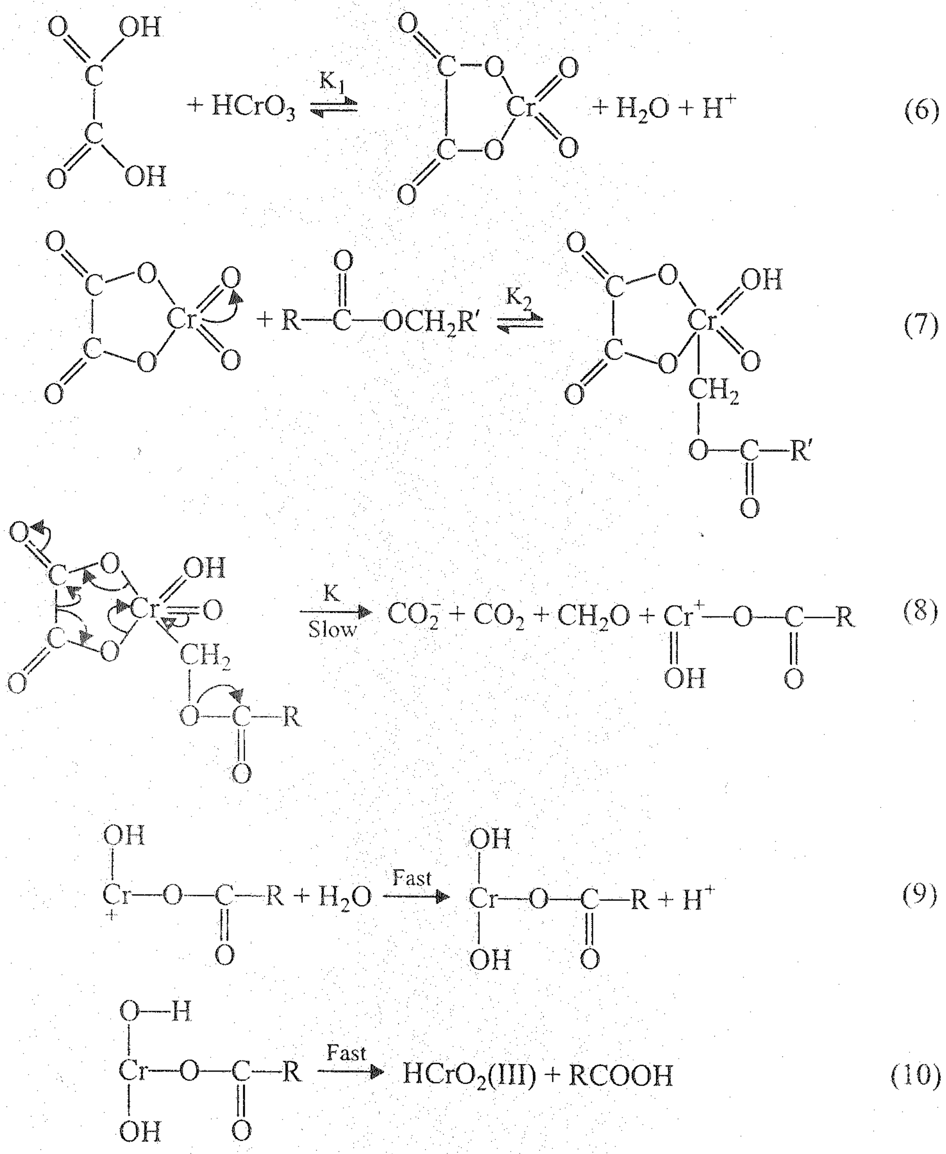
Fig. 4. Effect of varying [ester] with constant oxalic acid ([Cr(VI)] = 5 × 10^3 M, [H_2SO_4] = 3.0 M, [Oxalic acid] = 5 × 10^{-2} M, [HOAc] = 20% (v/v), Temp. = 35 ± 0.01°C)

TABLE-4

[Cr(VI)] = 5 × 10^{-3} M, [H_2SO_4] = 3.0 M, [Oxalic acid] = 5 × 10^{-2} M, [HOAc] = 20% (v/v), temperature = 35 ± 0.01°C

[ester] × 10^{-2} M	1/[ester]	Dimethyl malonate		Diethyl malonate	
		K × 10^{-2} min^{-1}	1/K	K × 10^{-2} min^{-1}	1/K
0.0200	50.000	10.730	0.0932	9.731	0.1028
0.0180	55.556	7.995	0.1251	8.662	0.1154
0.0160	62.500	6.244	0.1602	7.630	0.1311
0.0140	71.429	5.914	0.1691	6.246	0.1601
0.0125	80.000	5.185	0.1929	5.559	0.1799
0.0104	96.154	3.944	0.2535	4.576	0.2185

The rate of ester and oxalic acid taken together increases with increase in (H$^+$) showing HCrO$_3^+$ to be the likely reactive species. We can conclude that both the substrates take part in the oxidation reaction simultaneously; a three electron transfer mechanism is illustrated in **Scheme-2**.



Scheme-2

The rate law can be given as

$$\frac{-d[\text{Cr (VI)}]}{dt} = \frac{KK_1K_2\,[\text{Cr(VI)}][\text{OXH}_2][\text{Ester}]}{1 + K_1[\text{OXH}_2] + K_2[\text{Ester}]} \text{ in presence of oxalic acid}$$

This explain the first order dependence of rate on [Cr (VI)] and fractional order dependence on oxalic acid [OXH$_2$] and [ester].

The plots of 1/K *vs.* 1/[Ester] or 1/K *vs.* 1/[OXH_2] shows the fractional values of slopes (Table-5 and Fig. 5).

TABLE-5

[Cr(VI)] = 5×10^{-3} M, [H_2SO_4] = 3.0 M, [ester] = 5×10^{-2} M, [HOAc] = 20% (v/v), Temp. = 35 ± 0.01°C

[XOH_2] × 10^{-2} M	1/[XOH_2]	Dimethyl malonate		Diethyl malonate	
		K × 10^{-2} min^{-1}	1/K	K × 10^{-2} min^{-1}	1/K
0.0500	20.000	10.73	0.0932	10.940	0.0914
0.0450	22.222	7.833	0.1277	8.873	0.1127
0.0400	25.000	6.377	0.1568	7.079	0.1413
0.0350	28.571	5.914	0.1691	6.548	0.1527
0.0300	33.333	5.348	0.1870	5.962	0.1677
0.0250	40.000	4.320	0.2315	5.194	0.1925

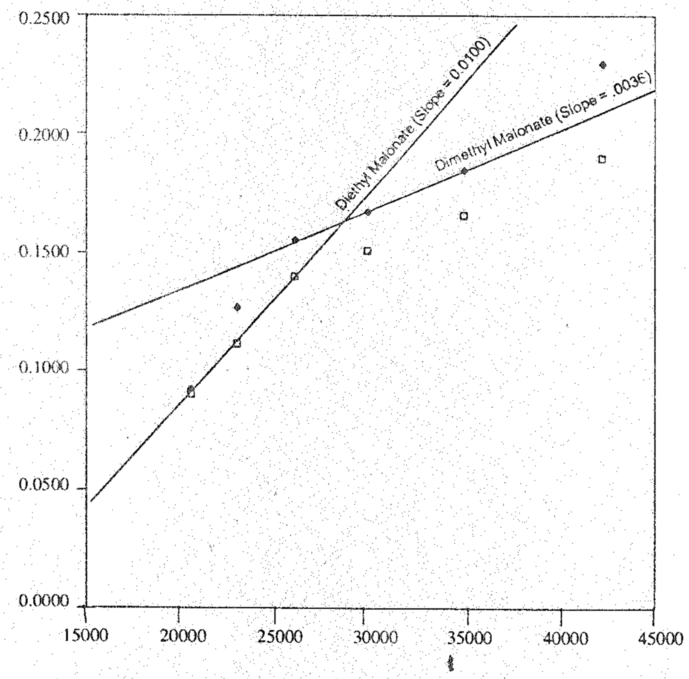


Fig. 5. Effect of varying [oxalic acid] with constant ester ([Cr(VI)] = 5×10^{-3} M, [H_2SO_4] = 3.0 M, [ester] = 5×10^{-2} M, [HOAc] = 20% (v/v), Temp. = 35 ± 0.01°C)

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