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KINETICS OF OXIDATION OF METHANOL AND MONO-DEUTERO-METHANOL BY CHROMIUM(VI) IN PERCHLORIC ACID MEDIUM

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Abstract—Kinetics of the oxidation of methanol and mono-deutero-methanol by Cr(VI) over a wide range of temperature (25–40°) have been studied in perchloric acid medium at constant ionic strength ($\mu = 1.0$ M) adjusted with sodium perchlorate. Each reaction is first order with respect to the substrate and dichromate concentrations but the order with respect to $[H^+]$ is nearly 3 in each case. Both these reactions take place at almost the same rate under identical experimental conditions. The activation parameters of the reactions are not widely different and the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the oxidation of methanol are 79.5 kJ mole^{-1} and -38.1 J deg^{-1} mole^{-1} respectively, whereas the corresponding values for the deuterated compound are 83.8 kJ mole^{-1} and -23.9 J deg^{-1} mole^{-1}. The probable mechanism of the reactions is discussed.

The chromic acid oxidations of a variety of organic compounds have been the subject of a large number of investigations.[1] Of these, the oxidation of isopropyl alcohol has been studied in detail by several investigators.[2–5] Most of the data show a decrease in rate constant with increase in gross chromium(VI) concentration.[6–8] This has been accounted for, considering that the acid chromate ion and not the dichromate ion is the effective oxidant, though the latter was reported[9] to oxidise inorganic compounds. Again methanol was found to be oxidised[10–12] by metal ions at a relatively slower rate than other mono-ols and the initial oxidation product was found to be formaldehyde irrespective of the rupture of O—H or C—H bonds. The present investigation on the oxidations of methanol and mono-deutero-methanol by chromic acid was undertaken in order to understand the mechanism of the reactions. Attempts were initially made to study the reactions at lower $[\mathrm{Cr(VI)}]_0$ of $\sim 10^{-4}$ M and $[H^+]_0 = 1.0$ M. The reaction was found to be too slow; but measurable rates were obtained at higher $[\mathrm{Cr(VI)}]_0$ ($> 3.0 \times 10^{-4}$ M).

EXPERIMENTAL

Reagents. Potassium dichromate (G.R., E. Merck), perchloric acid (B.D.H.) and sodium perchlorate (Riedel, Germany) were used. MeOH (E. Merck) was purified by refluxing with excess of freshly burnt quicklime, followed by distillation. MeOD (>99.9 atom % D) was of Fluka A. G. quality. All other reagents were chemically pure.

Kinetic measurements. Solns of the oxidant and the mixture containing organic substrate, perchloric acid and other chemicals (where necessary) were separately thermostated (±0.1°) for nearly 1 hr. The reaction was started by adding the oxidant to the mixture. The kinetics were followed iodometrically by removing aliquots after suitable intervals of time, quenching the reaction by adding it to an excess of KI soln and titrating the liberated I_2 by standard $Na_2S_2O_3$ aq, maintaining the appropriate acidity.

The reactions were carried out where the concentrations of the organic substrate and H-ion were much higher than that of the dichromate ion. Moreover, the ionic strength (maintained by $NaClO_4$, where necessary) and $[H^+]$ were assumed not to alter appreciably during the experiment. The pseudo-first-order rate constants were calculated from the slopes of log [Cr(VI)] vs. "time" plots. The duplicate experiments were reproducible to within ±3%. All measurements were carried out at 35°, unless otherwise stated.

Product analysis. MeOH was mixed with the oxidant in perchloric acid medium under the usual kinetic condition. The reaction was then allowed to proceed for several hours, and at definite intervals of time, aliquot parts were withdrawn and added to 2,4-DNP. The ppt thus obtained was filtered, washed and dried *in vacuo* (m.p. = 165–166°, lit. m.p.[13a] = 167°). The yields of the derivative are 96, 83, 60, 40 and 10% at 2, 4, 8, 12 and 24 hr respectively. These indicate that during kinetic investigation formaldehyde, which is obtained initially, is the major reaction product, but on standing further oxidation of formaldehyde to formic acid takes place.

RESULTS

Effect of variation of reactant concentration. The pseudo-first-order rate constants (k_{obs}) were calculated at various $[\mathrm{Cr(VI)}]_0$ but at constant $[\mathrm{substrate}]_0$, $[H^+]_0$, ionic strength ($\mu = 1.0$ M), and temp. The rate was found to increase with increase in $[Cr_2O_7^{2-}]$. The values of

$$\frac{k_{\mathrm{obs}}[\mathrm{Cr(VI)}]}{[Cr_2O_7^{2-}]}$$

at various [Cr(VI)] have been calculated at 35° and 45°. The results (Table 1) indicate that the dimeric species *viz* $Cr_2O_7^{2-}$, and not $HCrO_4^-$, is the effective oxidant. Similar observations have also been made in the oxidations of mono-deutero derivative.

The following equilibrium (1):

$$2HCrO_4^- \overset{K_d}{\rightleftharpoons} Cr_2O_7^{2-} + H_2O \qquad (1)$$

was used to calculate $[HCrO_4^-]$ and hence $[Cr_2O_7^{2-}]$, neglecting the subsidiary equilibrium (2)

$$HCrO_4^- \overset{K_d'}{\rightleftharpoons} H^+ + CrO_4^{2-} \qquad (2)$$

since $[H^+] \gg K_d'$, (1.75×10^{-6} at 35°). The value of K_d has been reported[13b] to be 76.0 at 35° and $\mu = 1.0$ M. At 45° no such data being available, K_d was ascertained by

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Table 1. Effect of oxidant on the oxidation of methanol

	35°				45°			
$[Cr(VI)]_0 \times 10^3$ M	$[HCrO_4^-] \times 10^3$ M	$[Cr_2O_7^{2-}] \times 10^3$ M	$k_{obs} \times 10^4$ (sec^{-1})	$k_{cor} \times 10^4$ (sec^{-1})	$[HCrO_4^-] \times 10^3$ M	$[Cr_2O_7^{2-}] \times 10^3$ M	$k_{obs} \times 10^4$ (sec^{-1})	$k_{cor} \times 10^3$ (sec^{-1})
0.667	1.137	0.0981	0.947	6.44	1.197	0.0685	1.78	1.73
1.34	2.045	0.3175	1.526	6.44	2.21	0.235	3.095	1.76
2.67	3.489	0.9255	2.232	6.44	3.89	0.725	4.79	1.77
3.34	4.111	1.2845	2.476	6.44	4.63	1.025	5.48	1.78
5.0	5.463	2.2685	2.921	6.44	6.25	1.875	6.62	1.76
6.67	6.639	3.347	3.231	6.44	7.68	2.83	7.38	1.74

$[MeOH]_0 = 1.0 \times 10^{-1}$ M, $[H^+]_0 = 1.0$ M.

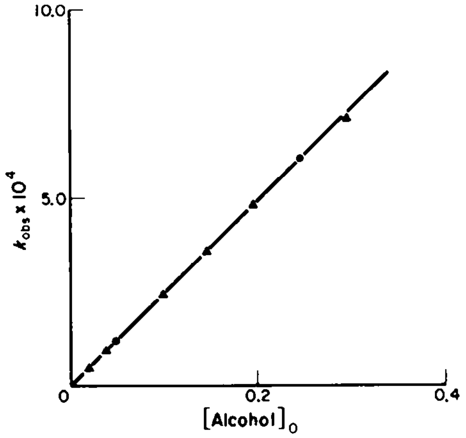


Fig. 1. Variation of pseudo-first-order rate constants with substrate concentrations. Plots of k_{obs} against $[alcohol]_0$ at 35°C. $[Cr(VI)]_0 = 3.34 \times 10^{-3}$ M, and $[H^+]_0 = 1.0$ M. ●, MeOH; ▲, MeOD.

interpolation of the reported data[14] at different temperatures. The K_d value so obtained is 48.0 at 45°.

The oxidations were also carried out at constant $[Cr(VI)]_0$, $[H^+]_0$ and temperature of 3.34×10^{-3} M, 1.0 M and 35° respectively, but at varied $[\text{organic substrate}]_0$ *viz* $(0.2–3.0) \times 10^{-1}$ M. The plot of k_{obs} vs $[alcohol]_0$ is linear passing through the origin (Fig. 1) showing that the intermediate compound formation is insignificant. The calculated quotients $k_{obs}/[alcohol]_0$ indicated that the order with respect to organic substrate is unity (Table 2).

Effect of $[H^+]$. The rate studies were made at different $[H^+]_0$, varied by the addition of perchloric acid. Since ionic strength had pronounced effect on the rate of reaction, the oxidation of the alcohols was carried out at constant ionic strength ($\mu = 1.0$ M), adjusted by the addition of sodium perchlorate. The rate of oxidation increases with the increase in acid concentration. The slope of log k_{obs} vs log $[H^+]_0$ plot (Fig. 2) is 2.8–2.9 for the oxidation of methanol and its mono-deutero derivative.

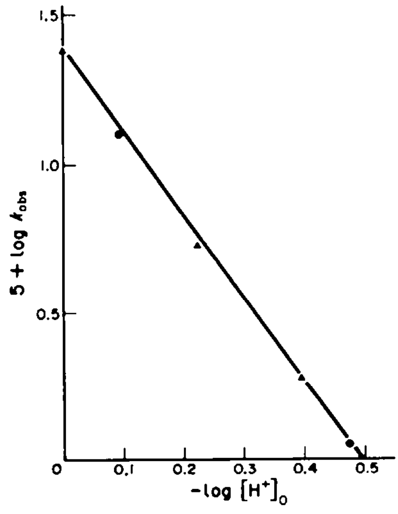


Fig. 2. Influence of $[H^+]_0$ on pseudo-first-order rate constants at constant ionic strength. Plot of log k_{obs} against log $[H^+]_0$. $[Cr(VI)]_0 = 3.34 \times 10^{-3}$ M, $[alcohol]_0 = 1.0 \times 10^{-1}$ M. $\mu = 1.0$ M and temp. = 35°C. ●, MeOH; ▲, MeOD.

Table 2. Effect of substrate concentration on reaction rates

[MeOH] × 10^1 M	$k_{obs} \times 10^4$ (sec^{-1})	k_{obs}/[MeOH] × 10^3 (l mole^{-1} sec^{-1})	Average k_{obs}/[MeOH] (l mole^{-1} sec^{-1})
0.2	0.48 (0.49)	2.40 (2.45)	
0.4	0.96 (0.96)	2.40 (2.40)	
0.5	1.21	2.42	2.40×10^{-3}
1.0	2.47 (2.40)	2.47 (2.40)	(2.41×10^{-3})
1.5	3.57 (3.60)	2.38 (2.40)	
2.0	4.80 (4.78)	2.40 (2.39)	
2.5	5.96	2.38	
3.0	6.98 (7.26)	2.33 (2.41)	

Figures in parentheses represent the values for monodeuteromethanol. $[H^+]_o = 1.0$ M, $[Cr(VI)]_o = 3.34 \times 10^{-3}$ M.

Effect of salts. Since chloride, sulphate and hydrogen phosphate ions inhibit[6] the rate of chromic acid oxidation of organic compounds, sodium perchlorate was used to study the effect of salts on the rate of the reaction. It has been noticed that the rate of the reaction increases with the increase in sodium perchlorate concentrations (Table 3) possibily due to the reaction between an ion and dipole.

Effect of $[Mn^{2+}]$. The pseudo-first-order rate constants were measured at $[\text{alcohol}]_o = 1.0 \times 10^{-1}$ M in the different concentrations of manganous ions (other conditions same as in Table 1). The pseudo-first-order rate constants decrease to nearly 50% (with $[Mn^{2+}]_o = 1.2 \times 10^{-3}$ M) of that in the absence of manganous ions in the oxidation of the alcohol, and the pseudo-first-order rate constant was independent at $[Mn^{2+}]_o > 1.2 \times 10^{-3}$ M. The addition of sodium perchlorate of the same strength does not influence the rate of oxidation.

Effect of temperature. The pseudo-first-order rate constants were determined at different temperatures. The values of second-order rate constants for the oxidations of methanol and monodeuteromethanol have been calculated at four different temperatures. The following equation

$$\log \frac{k_2}{T} = \left\{ \log \frac{k}{h} + \frac{\Delta S^{\ddagger}}{2.303\,R} \right\} - \frac{\Delta H^{\ddagger}}{2.303\,RT} \qquad (3)$$

(where k and h have their usual significances) was used to calculate the activation parameters. The least square plot of $\log k_2/T$ vs $1/T$ was used (Fig. 3) to calculate the enthalpy of activation ($\Delta H^{\ddagger}$), followed by the calculation of entropy of activation ($\Delta S^{\ddagger}$) from eqn (3). The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the oxidation of methanol are 79.5 kJ mole^{-1} and -38.1 J deg^{-1} mole^{-1} respectively, whereas the corresponding values for the deuterated compound are 83.8 kJ mole^{-1} and -23.9 J deg^{-1} mole^{-1}.

Table 3. Effect of salt concentration on the oxidation of methanol

[NaClO$_4$] × 10^1 M	$k_{obs} \times 10^4$ (sec^{-1})
0	2.47
0.8	2.74
1.6	2.95
2.4	3.20
3.2	3.75
4.0	4.04

$[MeOH]_o = 1.0 \times 10^{-1}$ M, $[H^+]_o = 1.0$ M, $[Cr(VI)]_o = 3.34 \times 10^{-3}$ M.

DISCUSSION

The reactions of methanol and monodeuteromethanol are similar in character, so they are believed to follow the same mechanism. The reactions are first order with respect to the oxidant and first order with respect to mono-ols, but the order with respect to acid is between 2 and 3. Since the rate of oxidation was found to increase with increase in $[Cr_2O_7^{2-}]$ and the values of

$$\frac{k_{obs}[Cr(VI)]}{[Cr_2O_7^{2-}]}$$

were practically the same at various gross [Cr(VI)], $Cr_2O_7^{2-}$ was considered as the reactive oxidant. In mono-ols having sp^3 hybridised O atom with two lone pairs directed towards the two corners of an irregular tetrahedron, +I effect of the Me group increases the electron density on the O atom. Hence mono-ols, acting as Lewis base, accept protons to form alkoxonium ion in the presence of high concentration of mineral acid (1.0 M). Unlike reactions at lower acidities (pH = 4.6) where molecular forms of mono-ols[10] reacted with the

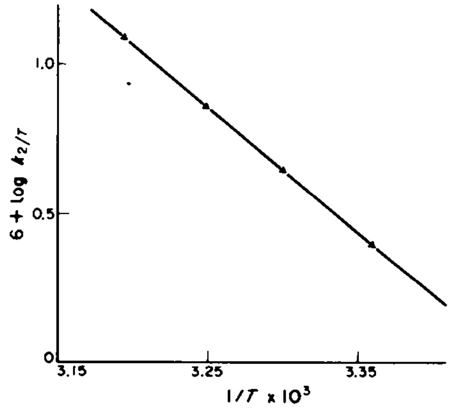
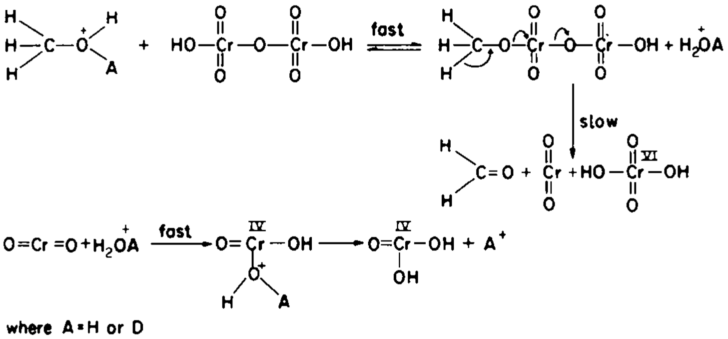
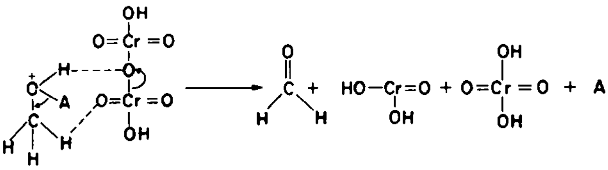


Fig. 3. Influence of temperature on second order rate constants. Plot of log k_2/T against $1/T$. $[Cr(VI)]_0 = 3.34 \times 10^{-3}$ M, $[\text{alcohol}]_0 = 1.0 \times 10^{-1}$ M and $[H^+]_0 = 1.0$ M. ●, MeOH; ▲, MeOD.



Scheme 1.



Scheme 2.

oxidant, oxidation of protonated mono-ols, i.e. alkoxonium ion in higher acid medium (1.0 M), is more likely.[12]

It is suggested that diprotonated $Cr_2O_7^{2-}$ reacts with the protonated mono-ols by a fast step to give an intermediate ester that then undergoes slow disproportionation to yield formaldehyde, $H_2Cr^{IV}O_3$ and $H_2Cr^{VI}O_4$ (Scheme 1). Cr (VI), therefore, behaves as a 2-equivalent oxidant. This is in keeping with the fact that addition of acrylamide to the reaction mixture failed to give any suspension, indicating that free radicals are not generated. Cr(IV) and Cr(VI), thus generated in the rate determining step, react rapidly to form Cr(V). This Cr(V) then oxidises mono-ols to give formaldehyde by a fast step.

$$Cr(IV) + Cr(VI) \rightarrow 2\,Cr(V)$$

$$2(CH_3OA + Cr(V) \rightarrow HCHO + Cr(III) + H^+ + A^+)$$

where, A = H or D. Cr(IV) may also disproportionate to give Cr(V) and Cr(III) followed by the reaction of the former with mono-ols to give products as shown below.

$$2\,Cr(IV) \rightarrow Cr(V) + Cr(III).$$

Alternatively, a bimolecular electron-switch mechanism, involving hydride ion transfer from the reactive substrate to the reactive oxidant may also be suggested (Scheme 2). This is in accordance with the suggestion of Rocek *et al.*[15] and was also supported by Graham and Westheimer[16] for strong acid medium. But the rates of oxidation of methanol and its monodeutero derivative under identical conditions, was found to be practically the same. The absence of kinetic isotope effect eliminated the possibility of O—A bond fission in the rate determining step. Hence the alternative mechanism seems to be unlikely.

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