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KINETICS AND MECHANISM OF OXIDATION OF ETHANOL, ISOPROPANOL AND BENZYL ALCOHOL BY CHROMIUM(VI) IN PERCHLORIC ACID MEDIUM

KALYAN KALI SENGUPTA,* TAPASHI SAMANTA and SAMARENDRA NATH BASU†
Department of Chemistry, Jadavpur University, Calcutta 700 032, India

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Abstract—Chromium(VI) oxidation of some alkanols has been studied in perchloric acid medium. The reactions are first order with respect to [substrate] and [$HCrO_4^-$]. The order with respect to [H^+] is between 1 and 2 for all the reactions. The activation parameters of the reactions have been calculated. A mechanism consistent with the above facts has been suggested. An attempt has been made to correlate the rate of the reactions with the structure of the substrates.

The chromic acid oxidations of some organic compounds have been investigated.[1–8] Most of the data show a decrease in rate constant with increase in gross $[Cr(VI)]_0$. But in methanol oxidation,[9] the dichromate ion has been found to be the reactive oxidant in perchloric acid medium. It was considered necessary to carry out similar reactions with other alkanols like ethanol, isopropanol and benzyl alcohol to see whether a similar mechanism operates or not. Moreover, we were interested to see whether there exists any correlation between the rate of reactions and the structure of the alcoholic moiety.

EXPERIMENTAL

Reagents. Potassium dichromate (G. R. E. Merck), perchloric acid (BDH) and sodium perchlorate (Riedel, Federal Republic of Germany) were used. Manganous perchlorate was prepared[10] by the reaction of manganous acetate with perchloric acid followed by recrystallization from perchloric acid. Alkanols (E. Merck) were purified by refluxing with excess of freshly burnt quicklime, followed by distillation. Mono-deutero-ethanol (> 99.9 atom % D) was of Fluka A. G. quality. All other reagents were chemically pure. Solutions were made in doubly distilled water.

Kinetic measurements. All the kinetic studies were conducted iodometrically as mentioned in our earlier communication.[9] The reactions were carried out at a $[Cr(VI)]_0$, $[H^+]_0$ and temperature of 3.34×10^{-3} M, 1.0 M and 35° and $[\text{ethanol}]_0$, $[\text{isopropanol}]_0$ and $[\text{benzyl alcohol}]_0$ were 1×10^{-1} M, 1×10^{-1} M and 5×10^{-3} M, respectively, unless otherwise stated. Most of the oxidation reactions involving benzyl alcohol were studied at much lower $[\text{substrate}]_0/[\text{oxidant}]_0$ ratios since this reaction is very fast under the conditions at which the other alkanols were oxidized. Ionic strength was kept constant by the addition of sodium perchlorate. The values of k_{obs} were reproducible to within ±3%.

Product analysis. The analysis of the products was carried out with the mixture, maintaining the kinetic conditions. The organic reaction products of ethanol, isopropanol and benzyl alcohol were confirmed by the preparation of their 2,4-DNP derivatives. After the kinetic experiments, 2,4-DNP was added to the mixture. The precipitates thus obtained were filtered, washed and dried *in vacuo*. [Acetaldehyde derivative yield 72%, m.p. 167–168° (lit.[11] m.p. 168.5°); acetone derivative yield 95%, m.p. 127.5° (lit.[11] m.p. 128°); benzaldehyde derivative yield 70%, m.p. 234° (lit.[11] m.p. 235°).] The products obtained in the oxidation of ethanol, isopropanol and benzyl alcohol failed[12] to give tests for acetic acid or benzoic acid although the primary oxidation products are known to be oxidized in their hydrated forms. The hydration equilibrium constants for formaldehyde, acetaldehyde and acetone only are available in the literature.[13a] These are 2.0×10^3, 1.3 and 2×10^{-3}, respectively, which indicate that if there is any further oxidation of formaldehyde, it is unlikely with acetaldehyde and acetone. Moreover, use of relatively much lower concentrations of oxidant in comparison to that of the alkanols, minimizes[13b] the possibility of further oxidation of the primary oxidation products, namely, the carbonyl compounds. Again, the relatively low yield of acetaldehyde and benzaldehyde in comparison to that of acetone may be due to the fact that in the presence of excess alkanols, the first oxidation product, namely, aldehydes and ketone are converted[13c] to their hemiacetal and hemiketal but the formation of hemiketal is less favoured due to steric and electronic effects.

RESULTS

Effect of variation of reactant concentrations

The pseudo-first-order rate constants (k_{obs}) were calculated at various $[Cr(VI)]_0$ but at constant $[\text{substrate}]_0$, $[H^+]_0$, ionic strength ($\mu = 1.0$ M) and temperature. The results recorded in Table 1 indicate that the rate decreases with an increase in initial gross Cr(VI) concentration. This is to be expected if $HCrO_4^-$ is the reactive species. The constancy of $k_{obs}[Cr(VI)]/[HCrO_4^-]$ was checked at various Cr(VI) concentrations, where Cr(VI) and $HCrO_4^-$ denote gross and reacting species of Cr(VI), respectively. The concentrations of $HCrO_4^-$ were calculated[14] from the relation

$$1/K_d = \frac{[HCrO_4^-]^2}{\{[Cr(VI)] - [HCrO_4^-]/2\}} \qquad (1)$$

assuming initial dimeric species as the gross Cr(VI) concentration. The value for the dissociation constant, K_d of the reaction

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

at 35° has been reported[15] to be 76.0 at $\mu = 1.0$ M. The pseudo-first-order rate constants (k_{obs}) were also ascertained at different $[\text{substrate}]_0$ but at constant $[Cr(VI)]_0$, $[H^+]_0$, ionic strength and temperature. The plots of k_{obs} against $[\text{alkanol}]_0$ indicate that the

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* Author to whom all correspondence should be addressed.

† Present address: Department of Chemistry, Asutosh College, Calcutta 700 026, India.

Table 1. Effect of oxidant concentrations on reaction rates

$[Cr(VI)]_t$ $\times 10^3$ M	$[HCrO_4^-]$ $\times 10^3$ M	$k^a_{obs} \times 10^3$ (s^{-1})	$k^a_{cor} \times 10^3$ (s^{-1})	$k^b_{obs} \times 10^3$ (s^{-1})	$k^b_{cor} \times 10^3$ (s^{-1})	$k^c_{obs} \times 10^3$ (s^{-1})	$k^c_{cor} \times 10^3$ (s^{-1})
0.677	1.137	2.40	1.41	2.02	1.18	4.80	2.82
1.34	2.045	2.13	1.40	1.83	1.20	4.27	2.80
2.67	3.489	1.83	1.40	1.54	1.18	3.69	2.83
3.34	4.111	1.67	1.36	1.48	1.20	3.49	2.84
5.0	5.463	1.54	1.41	1.32	1.2	3.09	2.83
6.67	6.639	1.37	1.38	1.20	1.20	2.82	2.83

a, ethanol; b, isopropanol; c, benzyl alcohol.

reaction is first order with respect to each [alkanol] (Fig. 1).

Effect of variation of perchloric acid concentration

The effect of variation of $[H^+]_0$ on the rate of oxidation was studied ($\mu = 1.0$ M). The oxidations were found to be acid catalyzed. The most widely used way of explaining their rate with acidity has been the Zucker–Hammett hypothesis,[16b,c] where log k_{obs} may be plotted against either log $[H^+]_0$ or $-H_0$, the Hammett acidity function. The plots of log k_{obs} against log $[H^+]_0$ are linear (Fig. 2) up to the acid concentrations studied. The slopes of the plots are 1.8, 1.9 and 1.3 for the oxidations of ethanol, isopropanol and benzyl alcohol, respectively. However, the reactions do not observe any simple order with respect to the Hammett acidity function, and the plot of log k_{obs} against $-H_0$ is not linear within the acid range studied. The values of the Hammett acidity function were taken from Rocek and Aylward.[16d]

Effect of variation of concentration of sodium perchlorate

The effect of variation of $[NaClO_4]_0$ on the rate of oxidation was measured at constant $[Cr(VI)]_0$, $[substrate]_0$, $[HClO_4]_0$ and temperature (Table 2). The rates were found to increase with increases in $[NaClO_4]_0$ from $(0.8–4.0) \times 10^{-1}$ M. This indicates that the reaction may involve ions of similar type or ion and dipolar species.[16e]

Effect of variation of concentration of Mn^{2+}

The reaction rates were studied in the presence of different concentrations of manganous ions. The results presented in Table 3 indicate that pseudo-first-order rate constants decreased to nearly 50% of that in the absence of manganous ion when $[Mn^{2+}] \geqslant 1.2 \times 10^{-3}$ M, in the oxidations of ethanol and isopropanol, whereas the decrease is nearly 25% for benzyl alcohol. The decrease in rate in the presence of manganous ion is therefore, in agreement with those reported earlier.[13a,14]

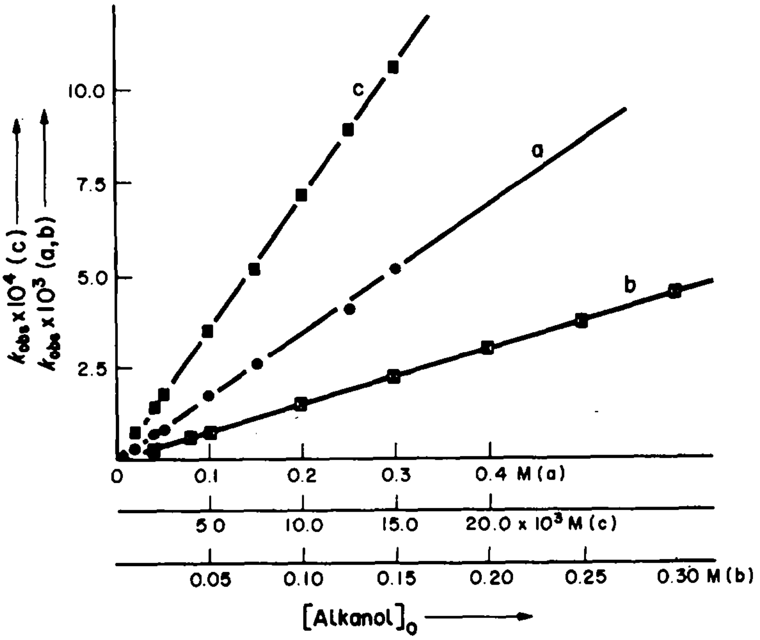


Fig. 1. Variation of pseudo-first-order rate constants with substrate concentrations. Plots of k_{obs} against $[alkanol]_0$. ●, ethanol; ☒, isopropanol; ■, benzyl alcohol.

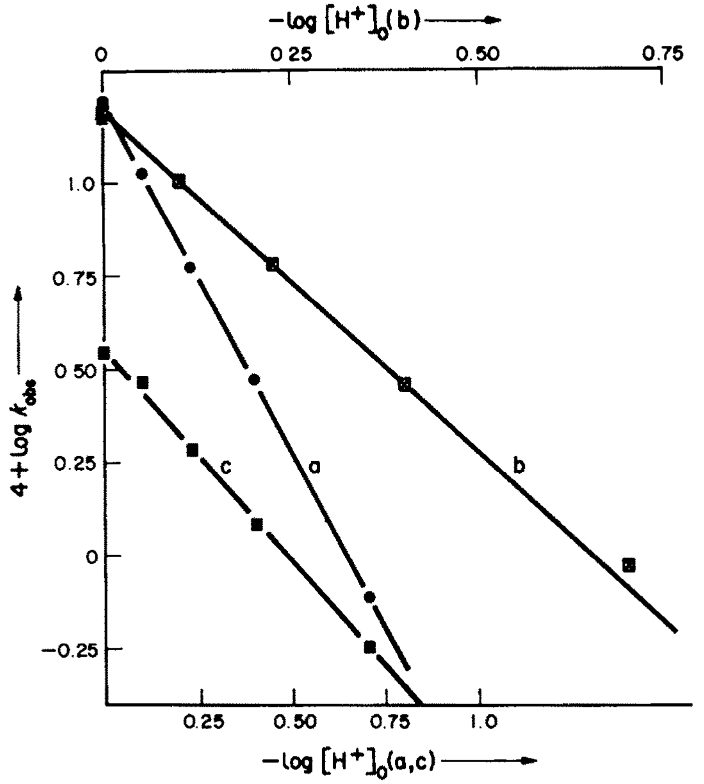


Fig. 2. Dependence of first-order rate constant on $[H^+]_0$. Plots of log k_{obs} against log $[H^+]_0$. ●, ethanol; ☒, isopropanol; ■, benzyl alcohol.

Activation parameters

The second-order rate constants (k_2) at different temperatures were calculated from the relation:

$$k_2 = k_{obs}/[\text{alkanol}]_0. \qquad (3)$$

The enthalpy of activation ($\Delta H^\ddagger$) was then calculated from the least squares plot of log (k_2/T) vs $1/T$ (Fig. 3) followed by the evaluation of entropy of activation ($\Delta S^\ddagger$). The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are recorded in Table 4. A linear isokinetic relationship[17] was obtained when $\Delta S^\ddagger$ was plotted against $\Delta H^\ddagger$ in the oxidations of alkanols.

DISCUSSION

The kinetics of oxidation of ethanol, isopropanol and benzyl alcohol are similar in character. Thus, all of them are first order with respect to $[HCrO_4^-]$ as well as [substrate] and the order with respect to $[H^+]$ is between 1 and 2. They are believed to follow a similar mechanism. This idea is also in keeping with the result of the isokinetic plot. Again, the autoprotolysis constants[18] for the alkanols are very small. At high acid medium (1.0 M) the concentration of alkoxide ion is very small. Consequently alkoxide ion cannot be considered as the reactive reductant. Moreover, alkanols, having lone pairs on oxygen atoms, can act as Lewis bases to accept one proton to form alkoxonium ion in the presence of a high concentration of mineral acids. Since the present reactions were carried out at high acidities (1.0 M), it is likely that an appreciable amount of each alkanol remains as alkoxonium ion ROH_2^+. The order with respect to acid (namely 1.3–1.9) can be explained by considering that the reactive oxidant and reductant are either H_2CrO_4 (formed by the reaction of H_3O^+ and $HCrO_4^-$) and the protonated alkanols or protonated H_2CrO_4 and the alkanol. If the oxidant is protonated then the order with respect to

Table 2. Effect of salt concentrations on reaction rates

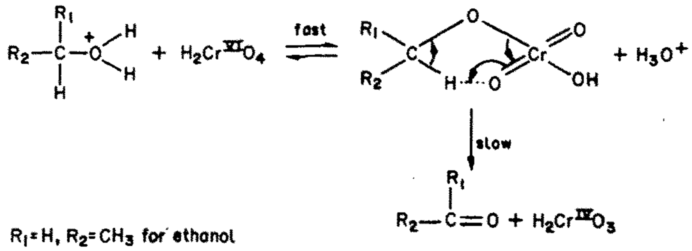
$[NaClO_4]_0 \times 10^1$ M	$k^a_{obs} \times 10^3$ (s^{-1})	$k^b_{obs} \times 10^3$ (s^{-1})	$k^c_{obs} \times 10^4$ (s^{-1})
0	1.67	1.48	3.49
0.8	1.71	1.54	3.67
1.6	1.79	1.67	3.84
2.4	1.92	1.75	4.08
3.2	2.08	1.83	4.36
4.0	2.26	1.92	4.68

a, ethanol; b, isopropanol; c, benzyl alcohol.

Table 3. Effect of manganese(II) ion concentrations on reaction rates

$[Mn^{2+}]_0 \times 10^3$ M	$k^a_{obs} \times 10^3$ (s^{-1})	$k^b_{obs} \times 10^3$ (s^{-1})	$k^c_{obs} \times 10^3$ (s^{-1})
0	1.67	1.48	3.49
0.4	0.96	1.01	3.14
0.8	0.92	0.91	2.86
1.2	0.87	0.79	2.67
1.6	0.87	0.79	2.67

a, ethanol; b, isopropanol; c, benzyl alcohol.



R_1 = H, R_2 = CH_3 for ethanol

R_1 = CH_3, R_2 = CH_3 for isopropanol

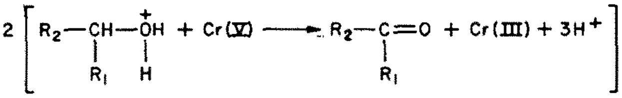
R_1 = H, R_2 = Ph for benzyl alcohol

acid must be the same for the oxidation of different alkanols. On the other hand, if the reductant is protonated then the order with respect to acid must be different for the oxidation of different alkanols. Actually the order is found to vary from 1.3 to 1.9 indicating that alkanols have been protonated. Moreover, the variation in rate, namely isopropanol > ethanol > benzyl alcohol conforms with the order of basicity of the alkanols. This supports the fact that chromic acid is not protonated but the alkanols are protonated. The reaction between H_2CrO_4 and protonated alkanols would be the preferred initial step since the rate of this reaction is expected to be enormously greater[19] than that involving protonated H_2CrO_4 (i.e. $HCrO_3^+$) and the neutral alkanols. Thus the reactive oxidant and reductant species are believed to be H_2CrO_4 and ROH_2^+. The increase in the rate of oxidation with an increase in ionic strength supports the involvement of an ion and a dipolar species.[16a]

The formation of the product is believed to proceed via the fast generation of an intermediate chromate ester stabilized by intramolecular H-bonding and subsequent slow disproportionation of ester to yield carbonyl compounds and $H_2Cr^{IV}O_3$. There is no direct kinetic evidence for the existence of such an ester, the equilibrium constant for the esterification process is believed to be very low. The mechanism of these oxidation reactions is given in the above scheme.

Cr(IV), generated in the rate determing step, reacts rapidly with Cr(VI) to form Cr(V), followed by the oxidation of more alkanol to the carbonyl compound in a fast step.

$$Cr(IV) + Cr(VI) \longrightarrow 2Cr(V)$$



$$2\left[R_2-\underset{R_1}{CH}-\underset{H}{\overset{+}{O}}H + Cr(V) \longrightarrow R_2-\underset{R_1}{C}{=}O + Cr(III) + 3H^+\right]$$

Cr(IV) may also disproportionate as

$$2Cr(IV) \longrightarrow Cr(V) + Cr(III).$$

Cr(V) then reacts with alkanols as shown above. The rates of oxidation of ethanol and its mono-deutero derivative under identical conditions were practically the same ($k_H/k_D \cong 1$). This is also in accordance with our earlier observation[9] from the oxidation of methanol and its mono-deutero derivative by Cr(VI).

The oxidation of alkanols by Cr(VI) leads to the formation of carbonyl compounds which can undergo further oxidation to alkanoic acids. Moreover, these alkanoic acids may form esters with excess alkanols in the presence of an inorganic acid catalyst. It is also known that oxidation of carbonyl compounds proceed via their hydrates.[20] These hydration reactions are catalysed by mineral acids.[21] Since the present investigation was carried out at 1.0 M acidity, the formation of alkanoic acid under the present experimental conditions is highly likely. The result of product analysis indicates the absence of alkanoic acid in the reaction mixture. It is possible that the carbonyl compound, the initial product, undergoes fast hemiacetal formation with excess alkanols rather than

Table 4. Activation parameters for the oxidation of alkanols

Alkanols	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$-\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
Ethanol	49.0	120.2
Isopropanol	53.2	107.7
Benzyl alcohol	26.6	180.8

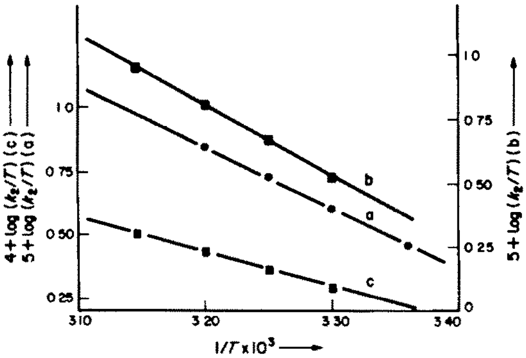


Fig. 3. Influence of temperature on second-order rate constants. Plots of log (k_2/T) against $1/T$. ●, ethanol; ☒, isopropanol; ■, benzyl alcohol.

hydration, in the presence of mineral acids acting as catalysts. Hemiacetal remains in equilibrium with carbonyl compounds which respond to the DNP test.

In consequence to the given mechanism, the substitution of the α-H of CH_3CH_2OH by a CH_3 group inhibits the formation of the intramolecularly H-bonded intermediate ester due to the $+I$ effect of the CH_3 group. Hence the rate of reaction is expected to be smaller with isopropanol in comparison to that of ethanol. Again the substitution of the CH_3 group of ethanol by a Ph group facilitates the formation of the intramolecularly H-bonded intermediate ester due to the $-I$ effect of the Ph group. Hence the rate of oxidation of benzyl alcohol is expected to be greater than that of ethanol. The actual order of the rate of reaction namely, benzyl alcohol > ethanol > isopropanol is in accordance with the suggested mechanism and establishes the fact that the rate of oxidation depends on the structure of the substrates.

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