COMMUNICATIONS

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by

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The Reduction of a Solution of Sodium Chromate in Hydrochloric Acid by Methanol

R. E. SOWDEN

ABSTRACT

The industrially interesting reduction by methanol of a solution of 0.8M sodium chromate in 6M hydrochloric acid has been investigated thermocalorimetrically. The proposed overall stoichiometric equation

$$2Na_2CrO_4(aq) + CH_3OH(aq) + 10HCl(aq) + H_2O(l) =$$
$$2[Cr(H_2O)_4 . Cl_2] . Cl(aq) + 4NaCl(aq) + CO_2(g)$$
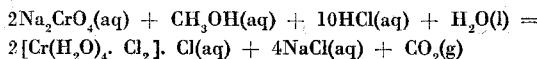
is in agreement with experimental observations at 21.2–70.8 °C. The molar ratio MeOH (consumed): CrVI (reduced)=1: 1.98 mol/mol; the mean heat of reaction, $\triangle H = -0.759$ MJ mol^{-1}; and carbon dioxide gas was proved to be evolved.

The experimentally determined activation energy, $E = 28.2$ kJ mol^{-1}, and the order of reaction with respect to methanol, $n = 1.81$, appear to be inconsistent with the chromate ester mechanism; an alternative reaction mechanism is suggested.

INTRODUCTION

It is known that aqueous solutions of chromic acid are readily reduced by organic reagents and that the reaction is catalysed by hydrogen ions [1]. There exist, however, few data in a form useful for process design purposes for the industrially interesting [2] reduction of a solution of sodium chromate in hydrochloric acid by methanol as a possible first step in the manufacture of anhydrous chromic chloride [3], CrCl$_3$, although the chromic acid oxidation of methanol in solutions of perchloric acid [4] and to a lesser extent sulphuric acid [5] have been studied previously.

MATERIALS

"AnalaR" grades of methanol and 36 per cent hydrochloric acid, and GRP grade anhydrous sodium chromate, were supplied by Hopkin and Williams Ltd [6].

APPARATUS

Experiments were carried out using a 500ml silvered glass calorimeter, vacuum insulated and fitted with a cotton wool bung and mercury in glass thermometer. As the limited aims of the present work did not include accurate measurements of heats of reaction, the more sensitive type of constant temperature environment isothermal calorimeter [7] with reactant ampoule and quartz crystal thermometer was not required.

Cooling corrections were determined over the temperature range 35–75 °C. The apparent constant of proportionality in Newton's law of cooling increased only slightly with increase in temperature from 35 to 60 °C but at an accelerating rate thereafter. The maximum operating temperature of the calorimeter was thereby limited to about 70 °C owing to the difficulty of monitoring cooling-rates in excess of $0.1 °C \ min^{-1}$.
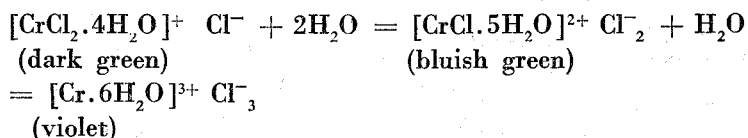
ANALYTICAL

Concentrations of CrVI in hydrochloric acid solution were determined by titration with 0.1N ferrous sulphate solution, using grease-free glass apparatus and PTFE taps. Orthophosphoric acid and sulphuric acid were added [8] to remove Fe III ions from solution as a colourless complex so that Fe II ions were oxidised prior to oxidation of the indicating amine, diphenylamine sulphonate. Direct oxidation of hydrochloric acid to chlorine by Cr VI was prevented by keeping the HCl concentration below 1M [9]. Potassium permanganate would have been unsuitable as a direct selfindicating titrant owing to its ability to oxidise HCl.

In the presence of Cr III, Cr VI in hydrochloric acid solution was precipitated with excess alkaline barium chloride and sodium acetate solution. Filtered in a sintered glass crucible and washed with distilled water, it was then re-dissolved in a minimum amount of 2M hydrochloric acid, diluted with an equal volume of distilled water and titrated with 0.1N ferrous sulphate solution as above.

Alternative analytical techniques were also considered. The potentiometric titration of a solution of 1M $FeCl_2$ in 5.6M HCl

against a solution of 0.9M Na_2CrO_4 in 6M HCl was found to give an endpoint in excellent agreement with theory, but electrode instability at intermediate stages of titration rendered it unsuitable as an analytical technique; this was possibly due to the kinetically slow hydrolysis of Cr III ions [10],[11]:

$[CrCl_2.4H_2O]^+$ Cl^- $+ 2H_2O$ $= [CrCl.5H_2O]^{2+}$ Cl^-_2 $+ H_2O$
(dark green)   (bluish green)
$= [Cr.6H_2O]^{3+}$ Cl^-_3
(violet)

Spectrophotometry has previously been used for the determination of Cr VI in a kinetic study of the cromic acid oxidattion of iso-propyl alcohol, but data points before 10% and after 90% complete reaction were erratic and had to be discarded [12]. In more recent investigations into the chromic acid oxidation of ethanol [13] and methanol [4] chemical analytical techniques were preferred.

EXPERIMENTAL PROCEDURE

Stoichiometry

Run 1: 20 ml of a solution of 10 % v / v methanol in 5.44M hydrochloric acid was quickly added to 165 ml of a well swirled solution of 0.837 M sodium chromate in 5.66M hydrochloric acid and allowed to react to completion. Concentrations of Cr VI were determined before and after reaction, and the temperature of the reacting solution was monitored.

Run 2: A blank solution of 0.747M sodium chromate in 5.70M hydrochloric acid was heated along the same temperature-time path as Run 1. Analysis of Cr VI present before and after heating showed that negligible direct reduction of Cr VI by hydrochloric acid had occurred; the maximum temperature reached was 70.8°C.

Kinetics

Runs 3–9: 165ml of a solution of 0.9M sodium chromate in 6M hydrochloric acid at 21–72°C was placed in the calorimeter and allowed to attain a steady rate of cooling. 20ml of a solution of 1.00 % v / v methanol in 6M hydrochloric acid solution at 21–68°C was then quickly added to the sodium chromate solution

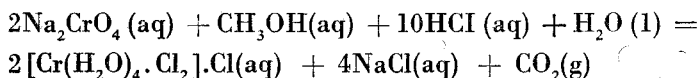and allowed to react to completion; meanwhile the temperature of the reacting soluion was monitored.

Physio-chemical properties of solutions

Heat Capacity: 20ml aliquots of a solution of 0.93M sodium chromate in 5.58M hydrochloric acid at ambient temperature were quickly added to 175ml of well swirled water at 41 and 65°C respectively; the temperature of the mixture was monitored during the two experiments. By setting up a pair of simultaneous heat balances and using values for the apparent molar heat capacity of aqueous HCl interpolated from available data [14], the heat capacity of the sodium chromate solution and the integral heat of dilution were found to be 3.17 kJ $l^{-1}°C^{-1}$ and –0.986 kJ l^{-1} respectively.

Heat of dilution of Cr VI in hydrochloric acid solution: 191.3g of 6.03M hydrochloric acid at 38°C was well swirled and 20ml of a solution of 0.937M sodium chromate in 5.58M hydrochloric acid quickly added; the temperature of the solution was monitored before and after mixing. The integral heat of dilution of the Cr VI solution determined from the heat balance was found to be only 0.59 kJ / litre of 6M HCl, and so was experimentally insignificant. Integral heats of dilution generally diminish with increasing concentrations of solute[15].

RESULTS AND DISCUSSION

The molar ratio of MeOH (consumed) to CrVI (reduced) was found to be 1:1.98 ($\pm 1\%$), indicating that the reduction of a solution of sodium chromate in hydrochloric acid by methanol can be represented in the temperature range 21.2–70.8°C by the overall stoichiometric equation (Equation 1):

$$2Na_2CrO_4 \text{ (aq)} + CH_3OH(aq) + 10HCl \text{ (aq)} + H_2O \text{ (1)} =$$
$$2[Cr(H_2O)_4.Cl_2].Cl(aq) + 4NaCl(aq) + CO_2(g)$$

The equation is analagous with overall stoichiometric equations reported for the reduction of a solution of chromic acid in sulphuric acid by methanol[5]:

$$2CrO_3 + CH_3OH + 3H_2SO_4 = Cr_2(SO_4)_3 + CO_2 + 5H_2O$$
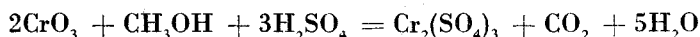
and for the reduction of a solution of Cr VI in mineral and organic acids by carbon monoxide gas in the presence of $H_2[PdCl_4]$ as homogeneous catalyst [16]:

$$Cr_2O_7^{2-} + 3CO + 8H^+ = 2Cr^{3+} + 3CO_2 + 4H_2O$$

Carbon dioxide gas was proved to be present in the off gases by bubbling nitrogen carrier gas through a reacting solution of 0.35M MeOH and 0.6M Na_2CrO_4 in 4.5M HCl, passing it demisted through ice-cold, de-aerated water to remove HCl gas, and then bubbling it into a saturated solution of limewater to form a dense white precipitate of calcium carbonate.

Equation 1 is also supported by thermochemical evidence: the mean experimental exothermic heat of reaction determined from Runs 1 and 3–9 (Table 1) was –0.759 MJ mol^{-1} which is within 3% of the theoretical value at 298 K calculated from available [17] thermodynamic data ($\Delta H_{298} = -0.778$ MJ mol^{-1}; $\Delta G_{298} = -0.846$ MJ mol^{-1}). The reaction is thus both strongly exothermic and thermodynamically feasible.

Methanol concentration versus time reaction profiles were derived from corrected temperature-time data (Runs 3–9) by means of the transformation:

$$[MeOH]_t = [MeOH]_0. (1 - \Delta T / \Delta T_{max})$$

A typical methanol concentration – time profile is illustrated in Figure 1.

The mean order of reaction with respect to methanol in the range 10–90% complete reaction at 21.2–68.6°C, using Van't Hoff's differential method [18]:

$$- d [MeOH] / dt = k. ([MeOH]_t - [MeOH]_\infty)^n$$
$$log(-d [MeOH] /dt) = n.log [MeOH] + log k$$

was found to be 1.81 ($\sigma = 0.17$) as shown in Table 1. Although the reaction is exothermic, deviations from isothermal conditions were experimentally insignificant because of the unusually low energy of activation.

The minimum concentration of hydrochloric acid necessary for a reasonably rapid rate of reaction to occur was observed to
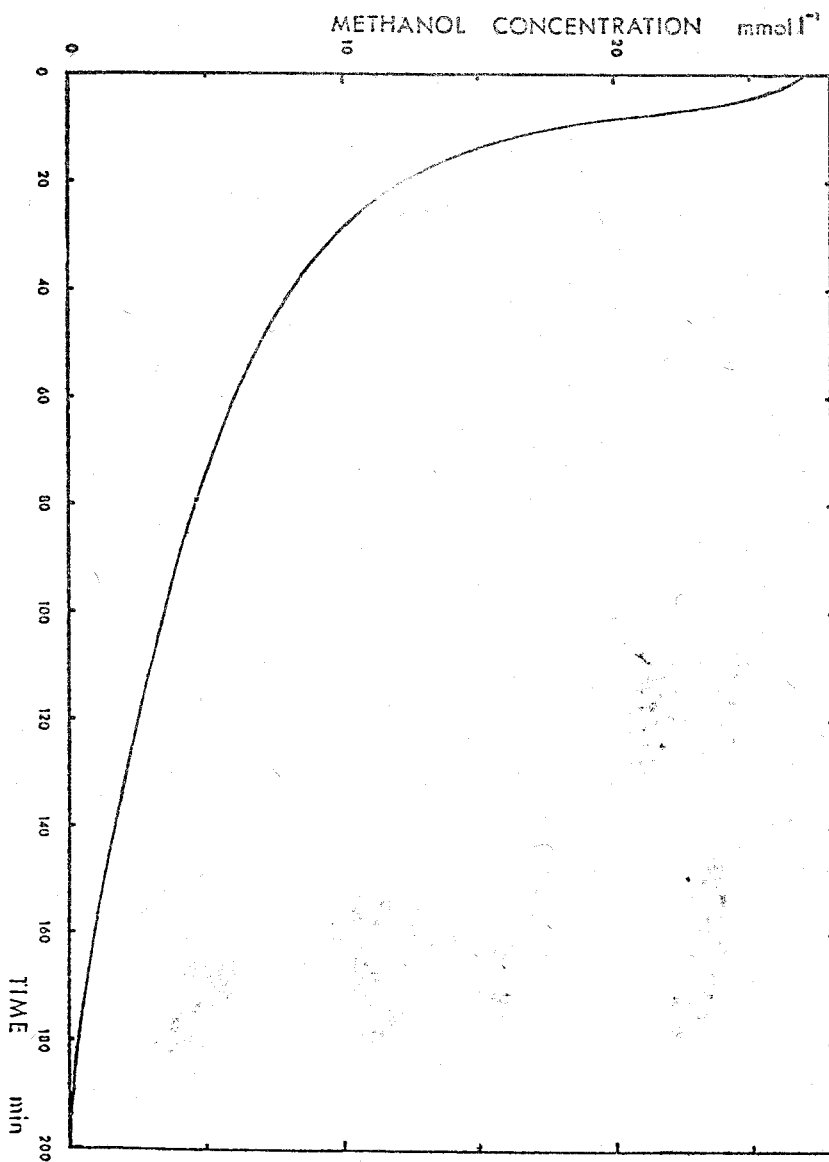
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Fig. 1. Typical reaction profile: methanol concentration vs. time of reaction

Table 1.

Run	Temperature °C	Heat of reaction MJ mol^{-1}	Order of reaction w.r.t. methanol
1	25.0–70.8	–0.710	
2	25.0–70.8		
3	21.2	–0.659	1.62
4	24.4	–0.751	1.66
5	28.9	–0.707	2.10
6	31.0	–0.698	1.73
7	48.3	–0.812	1.58
8	66.3	–0.922	2.44
9	68.6	–0.806	1.53
Mean		–0.759	1.81
Standard deviation		0.045	0.17

be about 1M, in agreement with the finding[19] that aliphatic primary alcohols are not significantly oxidised by refluxing with 1M aqueous sodium dichromate at pH5.6. 1M is therefore the maximum initial concentration of sodium chromate that can readily be reacted with methanol and 6M hydrochloric acid solution which, being close to the azeotropic composition at ambient temperatures, would simplify storage and handling operations on the large scale.

The energy of activation was calculated from Arrhenius' equation:

$$k = A \ e^{-E/RT}$$

by fitting the least squares straight line to:

$$\log k = \log A - E / 2.303RT$$

between 21.2 and 68.6°C in the range 10–90% complete reaction (Runs 3–9; Fig.2):

Activation energy, $E = 28.2. \times$ kJ mol^{-1}

Frequency factor, $A = 4.12 \times 10^6$ 1 mol^{-1} s^{-1}

Correlation coefficient, $r = 0.955$

Activation energies and frequency factors usually lie in the ranges 38–272 kJ mol^{-1} and $9 \times 10^9 \rightarrow 4.3 \times 10^{11}$ 1 mol^{-1} s^{-1} respectively [18]. Low values of E are sometimes attributable to diffusional control, but this is precluded in a homogeneous solution
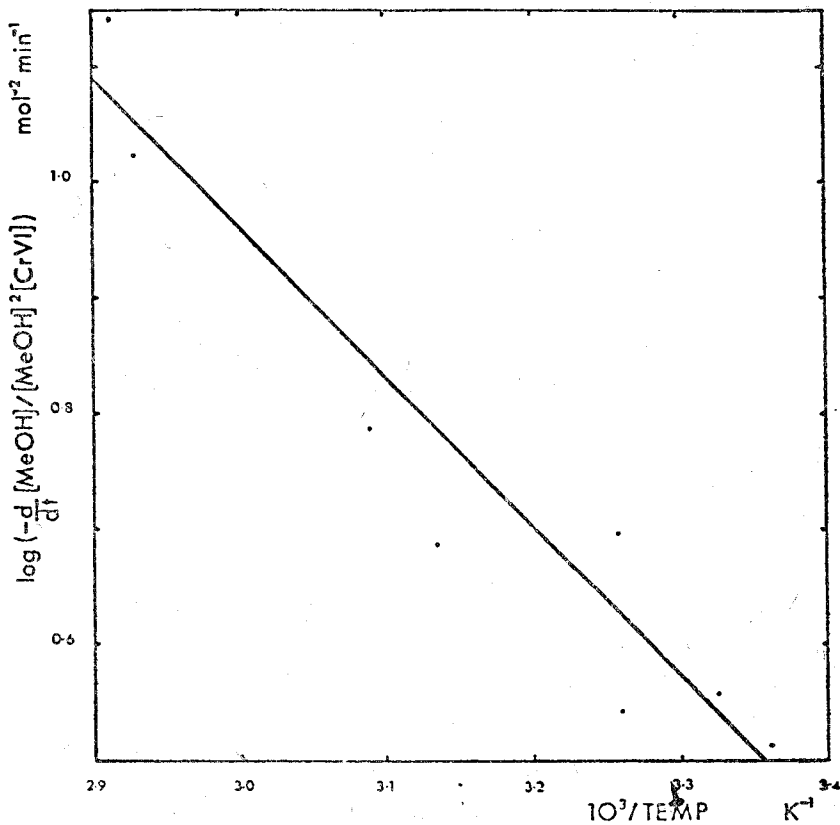
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Fig. 2. Arrhenius diagram: log (rate of reaction) vs. recipocal temperature

unless associated with extremely fast rates of reaction. Alternatively there may be an exothermic equilibrium step whereby the increase in the rate of forward reaction induced by a rise in temperature is largely offset by depression of the eqilibrium constant, K_c, by analogy with Van't Hoff's equation:

$$d(\ln K_c) / dT = \Delta H / RT^2$$

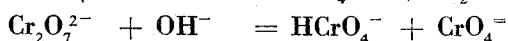for: $\Delta H > 0.$

Mechanism of reaction

Ionic aquilibria: Chromium trioxide dissolves readily in water, dissociating in accordance with pH-dependent equilibria [10]:

$$H_2CrO_4 \quad = HCrO_4^- + H^+ \quad (K_1 = 4.1)$$
$$H\ CrO_4^- = CrO_4^{2-} + H^+ \quad (K_2 = 10^{-5.9})$$
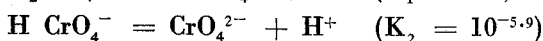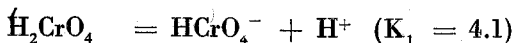
The primary acid is strongly dissociated but the secondary acid, favoured by low CrVI concentrations, is only weakly dissociated. At higher CrVI concentrations and low pH values the orange-red dichromate ion is formed by polymerisation:

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \quad (K = 10^{2.2})$$
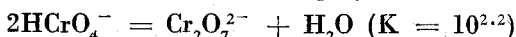
Base hydrolysis reactions may also occur:

$$HCrO_4^- + OH^- = CrO_4^= + H_2O$$
$$Cr_2O_7^{2-} + OH^- = HCrO_4^- + CrO_4^=$$

The overall equilibrium has been determined spectrophotometrically (ionic strength, 0.375M; pH5. 26 — 6.33; 25°C):

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O \quad (K = 1.3 \times 10^{16})$$
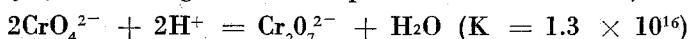
The concentration of $HCrO_4^-$ was reported to be 3% [20].

The main species existing in Cr VI solutions of varying acidity are summarised in Table 2. The above considerations, however, pertain only to solutions of Cr VI in perchloric acid or nitric acid. In the presence of hydrochloric acid or sulphuric acid, as in the present work, chlorochromate and sulphatochromate complex ions are formed almost quantitatively [10].

Table 2.
Main Cr VI species existing in aqueous solutions of varying acidity

pH of solution	Main Cr VI species
1	H_2CrO_4
2–6	$HCrO_4^-$ in equilibrium with $Cr_2O_7^{2-}$
6	CrO_4^{2-}

$$CrO_3(OH)^- + H^+ + Cl^- = CrO_3Cl^- + H_2O$$
$$CrO_3(OH)^- + HSO_4^- = CrO_3(OSO_3)^{2-} + H_2O$$
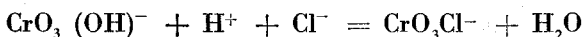
Equilibrium constants have been determined (0.5M and 1.0M HCl; 25°C) [21]:

$$H_2CrO_4 + Cl^- = CrO_3Cl^- + H_2O \quad (K = 10^{2.0})$$
$$HCrO_4^- + Cl^- = CrO_3Cl^- + H_2O \quad (K = 10^{1.2})$$

The stability of chlorochromate and sulphatochromate ions in acidic solution depends on the kinetically slow rate of oxidation of halide ions by dichromate ions at normal temperatures.

In the system under study the calculated initial conditions are:

$$[CrO_3Cl^-] \; / \; [H_2CrO_4] \quad = 500 \; mol/mol$$
$$[CrO_3Cl^-] \; / \; [HCrO_4^-] \quad = 464 \; mol/mol$$

Hence, only 0.2% of the Cr VI exists in solution as undissociated H_2CrO_4, 0.2% as $HCrO_4^-$ and less than 0.1% as $Cr_2O_7^{2-}$; and yet the reduction of Cr VI was observed to be rapid.
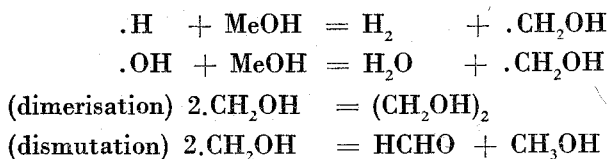
Chromate ester mechanism: It has been emphasised in a critical review of chromic acid oxidation processes[1] that the chromate ester mechanism proposed [12] for the chromium trioxide oxidation of isopropyl alcohol with perchloric acid should not be assumed to apply to other chromic acid oxidation reactions. Furthermore, it was suggested that direct removal of hydride ion from an alcohol undergoing oxidation may occur, and that free radical intermediates are a possibility except in the first step in the reaction. More recent support for the chromate ester mechanism has been provided in the case of dilute chromic acid oxidation of ethanol with perchloric acid[13], in which small amounts of NaCl accelerated the reaction by as much as 5%, and also with the chromic acid-methanol-perchloric acid system (0.002M CrO_3 0.23M $HClO_4$; ionic strenghth, 0.4)[4].

The results obtained in the latter work differ significantly from those now reported, indicating that the chromate ester mechanism does not apply in the sodium chromate-methanol-hydrochloric acid system (see Table 3). This is probably because the chromate ester mechanism assumes that the important Cr-containing species are $HCrO_4^-$, Cr^{5+}, Cr^{4+}, Cr^{3+}, and Cr^{2+}, whereas the major Cr-species in the hydrochloric acid system is CrO_3Cl^-, with relatively low concentrations of H_2CrO_4, $HCrO_4^-$ and $Cr_2O_7^{2-}$.

Table 3.
Comparison of data for the chromic acid oxidation of methanol

Source ot date	Order of reaction w.r.t. methanol concentration	Apparent Arrhenius activation energy kJ mol^{-1}
[4]	1	46–50
present work	1.8	28

A possible reaction mechanism : The radiolytic decomposition products ofaqueous methanol suggest several organic intermediates that might occur in the present system, particularly formaldehyde and ethylene glycol, which are apparently formed by rapid abstraction of a proton from the α–carbon atom of the methanol by free .H and .OH radicals (derived from the radiolytic decomposition of water [22]) followed by either dimerisation or dismutation of the free methyl hydroxy radical:

$$.H \; + MeOH \; = H_2 \qquad + \; .CH_2OH$$
$$.OH + MeOH = H_2O \qquad + \; .CH_2OH$$
$$(dimerisation) \; 2.CH_2OH \quad = (CH_2OH)_2$$
$$(dismutation) \; 2.CH_2OH \quad = HCHO + CH_3OH$$

In the presence of oxidising agents the radiolytic yields of formaldehyde and ethylene glycol are markedly increased and decreased respectively [9]; probably a reaction similar to that occurring in the presence of low concentrations of ferric ions [22] takes place:

$$.CH_2OH + Fe^{3+} = Fe^{2+} + HCHO$$
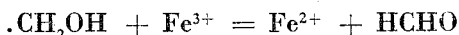
Indeed, the only decomposition product detected when aqueous ethanol is irradiated in the presence of air is acetaldehyde [23].

Comparable processes may well occur in the presence of Cr VI. Certainly acetaldehyde and acetone are the principal products when dilute aqueous solutions of ammonium dichromate containing ethanol and iso-propanol undergo photolysis [24].
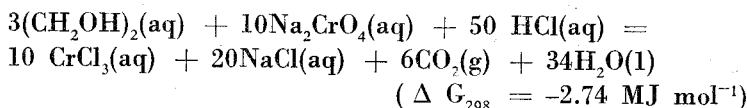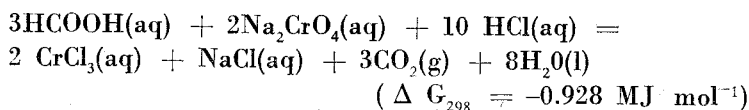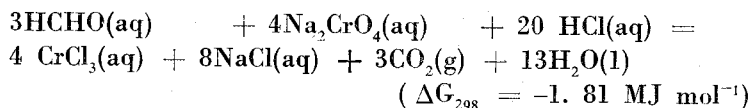
A proton can also be extracted from formaldehyde by photolysis [25] if sufficient energy is applied:

$$HCHO \quad = .H + .CHO$$
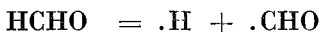
It was confirmed in the present work by visual comparison of rates of reaction (orange → burgundy → brown), using solutions of 0.33M MeOH, 0.33M HCHO, 0.33M HCOOH and 0.16M $(CH_2OH)_2$ with aliquots of a solution of 0.42M sodium chromate in hydrochloric acid, that three likely organic intermediates, formaldehyde, acetic acid and ethylene glycol, all react exothermically and do so faster than methanol in the sequence:

$$HCHO > HCOOH > (CH_2OH)_2 > CH_3OH$$
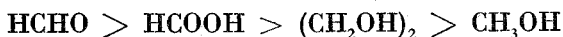
The calculated changes in free energy are large and negative for the theoretical stoichiometric equations derived by analogy with Equation 1:

$$3HCHO(aq) \quad + 4Na_2CrO_4(aq) \quad + 20 \ HCl(aq) \ =$$
$$4 \ CrCl_3(aq) + 8NaCl(aq) + 3CO_2(g) + 13H_2O(l)$$
$$(\ \Delta G_{298} \ = -1. \ 81 \ MJ \ mol^{-1})$$

$$3HCOOH(aq) + 2Na_2CrO_4(aq) + 10 \ HCl(aq) \ =$$
$$2 \ CrCl_3(aq) + NaCl(aq) + 3CO_2(g) + 8H_2O(l)$$
$$(\ \Delta \ G_{298} \ = -0.928 \ MJ \ mol^{-1})$$

$$3(CH_2OH)_2(aq) + 10Na_2CrO_4(aq) + 50 \ HCl(aq) \ =$$
$$10 \ CrCl_3(aq) + 20NaCl(aq) + 6CO_2(g) + 34H_2O(l)$$
$$(\ \Delta \ G_{298} \ = -2.74 \ MJ \ mol^{-1})$$

The calculated change in free energy for the direct oxidation of hydrochloric acid by sodium chromate:

$$Na_2CrO_4(aq) + 8HCl(aq) \ =$$
$$1\tfrac{1}{2} \ Cl_2 \ (g) + CrCl_3(aq) + 2NaCl(aq) + 4H_2O(l)$$
$$(\ \Delta \ G_{298} \ = -37.5 \ kJ \ mol^{-1};$$
$$\Delta H_{298} \ = 44.3 \ kJ \ mol^{-1})$$
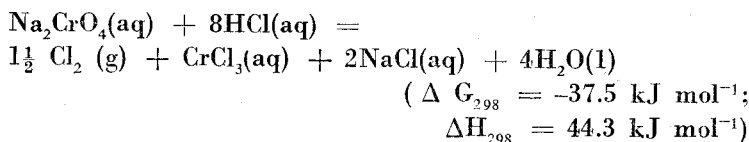
a reaction which occurs under boiling conditions, is in contrast small and negative, and the reaction is slightly endothermic. Presumably that is why this side reaction appears to be relatively sensitive to changes in temperature.

A reaction mechanism is described in Fig. 3 in which (i) the overall order of reaction with respect to methanol appears to be about 2, (ii) all the species invoked are known to exist, (iii) the overall stoichiometry is in agreement with experiment (1 MeOH: 2 Cr VI), and (iv) the suggested organic intermediate, formaldehyde, reacts faster than methanol. In this model, if the initial H-abstraction were fast but the subsequent dismutation of two methyl hydroxy radicals were slow and rate-determining there might be an induction period of apparent order unity in which the formaldehyde concentration would increase until sufficiently great to sustain a rapid rate of reaction. Both HCHO and H_2CrO_4 concentrations would thus be low initially: an induction period was noted in the present work. The slow dismutation step might

also be the exothermic equilibrium reaction responsible for the observed low activation energy of the reaction.

Further investigations into the mechanism of reaction could usefully include visible region spectrophotometry to determine CrIII and CrVI concentrations, ultraviolet spectrophotometry to identify any charge transfer complexes of the type $Cr^{III--VI}$, and electron spin resonance to identify Cr IV and Cr V, both of which are reported as being intermediates in the reduction of aqueous Cr VI by ferrous and other common ions[10].
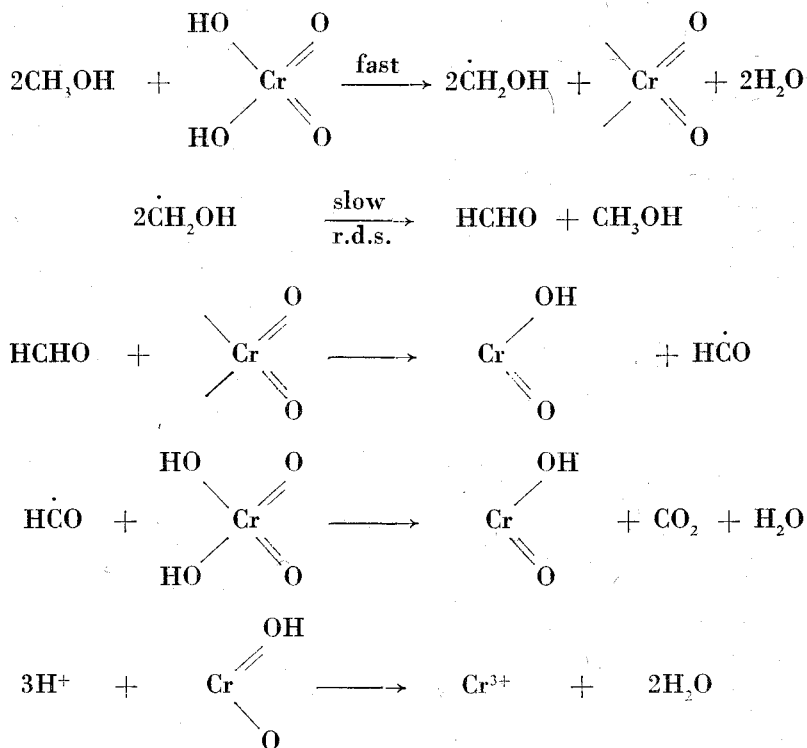

Fig. 3 A possible reaction mechanism

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ÖZET

0,8M sodyum kromatın 5 M hidroklorik asitteki çözeltisinin indüstiryel açıdan ilgi çekici olan metanol ile indirgenmesi, termodinamik olarak araştırılmıştır. Teklif edilen stokyometrik denklem:

$$2Na_2CrO_4(aq) + CH_3OH(aq) + 10HCl(aq) + H_2O(l) =$$
$$2[Cr(H_2O)_4.Cl_2].Cl(aq) + 4NaCl(aq) + CO_2(g)$$
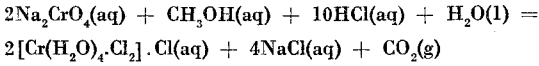
21,2–70,8 °C arasında yapılan deneysel gözlemlere uygundur. Molar orantı, MeOH (harcanan): Cr VI (indirgenen)=1:1, 98 mol/mol; ortalama reaksiyon ısısı $\triangle H = -0,759$ MJ mol^{-1}, karbondioksidin çıktığı da ispatlanmıştır.

Deneysel olarak tayin edilen aktifi kasyon enerjisi, E =28,2 kJ mol^{-1} ve metanola göre reaksiyonun mertebesi, n = 1,81; Kromat ester mekanizmasıyla bağdaşır görünmemektedir. değişik bir mekanizma teklif edilmektedir.