Kinetics And Mechanism Of The Reduction Of Dichromate Ion By 2-Methyl Pentane-2,4-Diol In Aqueous Hydrochloric Acidic Medium

S. O. Idris*, J. F. Iyun and E. B. Agbaji
Department of Chemistry, Ahmadu Bello University, Zaria , Nigeria.

ABSTRACT

The stoichiometry and kinetics of the reduction of dichromate ion by 2-methylpentane-2,4-diol have been investigated in aqueous hydrochloric acid medium at 27 ±1 °C. The reaction is first order with respect to oxidant and reductant concentrations and also acid dependent. The empirical rate law conforms to the rate equation:

$$\frac{1}{2}\frac{d[Cr^{3+}]}{dt} = a[H^+][pen\tan ediol][Cr(VI)]$$

The result of spectroscopic investigation and kinetic studies did not indicate intermediate complex formation. An outer sphere pathway is proposed for this reaction.

INTRODUCTION

Oxidative properties of Cr(VI) are of considerable importance in both analysis and oxidation of organic and inorganic substrates [1,2,3]. Cr (VI) in water exists as CrO_4^{2-}, $HCr_2O_7^{2-}$ and $H_2Cr_2O_7$ [2,4]. Of all these species, $HCrO_4^-$ has been identified as the only active oxidizing species in aqueous acidic solution [1,2,5,6,7]. Although some kinetic information has been published on the oxidation of secondary alcohol by Cr(VI) [1,2, 8-16] complementary studies on its possible reaction pathways are scanty. It is in the light of this that the present work was undertaken with the aim of providing relevant information on the plausible mechanism for the electron transfer reaction of 2-methylpentane-2,4-diol .

EXPERIMENTAL

Materials

2-methylpentane-2,4-diol (BDH) hereafter referred to as diol was used as supplied in making its standard solution. Sodium dichromate solution in distilled water was then standardized using titrimetric method[17]. A stock solution of HCl was prepared by diluting the commercial acid (M&B) and the solution was standardized titrimetrically using sodium carbonate. Stock solutions of sodium methanoate, sodium chloride and sodium ethanoate were prepared from Analar grade salts.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of $Cr_2O_7^{2-}$ was kept constant at 0.007 mol dm^{-3} while that of diol was varied between 0.001 and 0.036 mol dm^{-3} at $[H^+]$ = 0.6 mol dm^{-3} and constant ionic strength (NaCl). The reactions were allowed to stand until the repeated absorbances of the solutions at λ_{max} = 580 nm were constant. The stoichiometry was then determined from the plot of the absorbance versus [diol].

Kinetic studies

The rate of the reaction was monitored on a Corning Colorimeter 253 by observing the rate of increase of absorbance of the product at 580 nm. All kinetic measurements were conducted under pseudo-first order conditions with the diol concentration in at least 30-fold excess over the $[Na_2Cr_2O_7]$ at 27±1°C.

Acid dependence studies

The effect of acid on the rate of the reaction was determined by keeping all other conditions constant while varying the acid concentration in the range of $0.4 \le H^+ \le 0.8$ mol dm^{-3}.

Effect of ionic strength

The influence of ionic strength on the rate of the reaction was studied over the range 0.6 - 1.2 mol dm^{-3} using NaCl as the inert electrolyte while keeping other conditions constant.

Influence of added anions

The effects of added methanoate and ethanoate ions on the rate of reaction were investigated by varying the concentration of these anions while keeping $r_2O_7^{2-}]$, [diol] and ionic strength constant.

RESULTS AND DISCUSSION

Stoichiometry and product analysis

The stoichiometry of the reaction between diol and dichromate ion was found to be 1:3. A similar stoichiometry was reported for the reaction between the oxidant and isopropyl alcohol[2] or pinacol[12, 18].

The colour of the product with λ_{max}=580 nm is blue-green which indicates the presence of Cr^{3+} in the mixture. The ether extract of the product obtained by reacting stoichiometric amounts of reactants at $[H^+]=0.6$ mol dm^{-3} was subjected to conventional functional group tests[19], infrared spectroscopy and thin layer chromatographic analyses.

The product extract gave a precipitate with 2,4-dinitrophenylhydrazine, negative result for Fehling's test and positive result with Tollen's reagent suggesting that the product contained ketonic functional group. The broad spectrum at 3447.76 cm-1 was assigned to -OH. The peaks at 2858 - 2977.05 cm^{-1} indicated symmetrical and antisymmetrical stretching of CH_2 and symmetric stretching of CH_3. C = O stretch due to ketonic functional group occurred at 1731.22 cm^{-1}. These peaks are in agreement with values reported in the literature for ketone and hydroxyl functional groups[20].

The ether extract of the product and 2-methylpentane-2,4-diol solution were analysed by comparative thin layer chromatography (tlc). Each of these was spotted on already prepared plate using petroleum ether:ethyl acetate (3:2) and butanol; acetic acid and water (4:1:5) as mobile phases. The spots were located by irradiation of the plate with ultraviolet light. 2-methylpentane-2,4-diol was not moved at all from the base line, but the product moved as a single spot. This suggests the absence of 2-methylpentane-2,4-diol in the product. On the basis of these results, 4-hydroxy-4-methyl pentane-2-one is proposed as the name of the organic product of this reaction and the stoichiometry is given as:

$$Cr_2O_7^{2}+3CH_3C(OH)(CH_3)CH_2CH(OH)CH_3+8H^+ \rightarrow 2Cr^{3+}+3CH_3C(OH)(CH_3)CH_2COCH_3+7H_2O \quad \ldots\ldots(1)$$

Rate law

Pseudo-first order rate constants (k_1) obtained from plots of log (A_∞ - A_t) versus time (where A_t and A_∞ are the absorbances at time, t and the end of reaction respectively) showed a linear dependence on diol concentration at constant [H^+]. The first order in [diol] was confirmed by plotting k_1 versus [diol], which was linear and passed through the origin. The second order rate constants (k_2) were obtained from k_1 as k_1/[diol]. The calculated values of k_2 in each case were fairly constant (Table 1). Thus the rate of the reaction is:

$$\frac{1}{2}\frac{d[Cr^{3+}]}{dt} = k_2[pen\tan ediol][Cr(VI)]$$

……………..................……………(2)

$k_2 = 1.71 \pm 0.04 \times 10^{-3}\ dm^3\ mol^{-1}s^{-1}$

Acid dependence

A plot of k_2 versus [H^+] was linear without intercept indicating that k_2 varies with [H^+] according to equation (3).

k_2=a[H^+]………… (3)

$a = 3.40 \times 10^{-3}\ dm^6\ mol^{-2}s^{-1}$

When the expression for k_2 in the equation (3) is substituted into equation (2), the rate equation for the reaction becomes:

$$\frac{1}{2}\frac{d[Cr^{3+}]}{dt} = a[H^+][pen\tan ediol][Cr(VI)]$$

…………...………………………(4)

Anion dependence

The results as presented in Table 2 show that methanoate and ethanoate anions retarded the reaction rate. Chloride ion has been reported to inhibit the chromic acid oxidation of isopropyl alcohol in acetic acid aqueous medium[21]

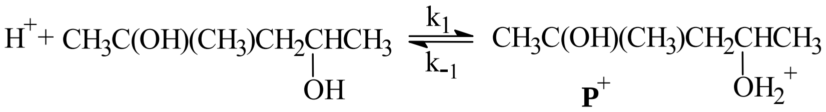
Ionic strength dependence

The result as presented in Table 1 shows that the rate decreases with increase in ionic strength suggesting a negative Bronsted - Debye salt effect. This is synonymous with a reaction occurring between oppositely charged species [22-24].The plot of log k_2 versus square root of ionic strength was linear with a slope of -0.52, an indication that some other interactions might have taken place to account for the non-integral value of the slope.

Reaction mechanism

The rate of reductions of many oxyanions usually indicates strong dependence on [acid] [1,2,9,11,12,14,25-29]. The [H^+] dependence on the rate may not be unconnected with the various equilibria established in an aqueous solution of chromic acid. The H^+ consumption must be as a result of conversion of oxoanions to a hydrated cation, $Cr(H_2O)_6^{3+}$. Therefore, it is not surprising that rates of the reaction increased with increase in [H^+]. The first order in diol concentration observed in our studies is similar to that observed in chromic acid oxidation of isopropyl alcohol[2] and oxidation of leucomalachite green by Cr(VI)[7].

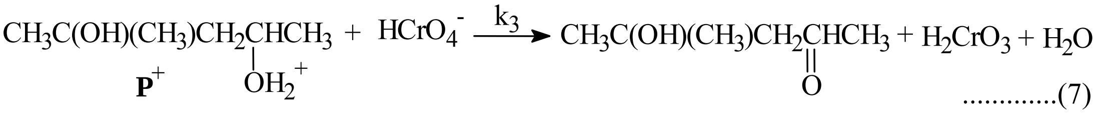
On the basis of the evidence so far adduced, the following scheme is hereby proposed for the title reaction.



$$H^{+} + CH_3C(OH)(CH_3)CH_2\underset{\substack{|\\ OH}}{C}HCH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{P^{+}}}{CH_3C(OH)(CH_3)CH_2}\underset{\substack{|\\ OH_2^{+}}}{C}HCH_3$$

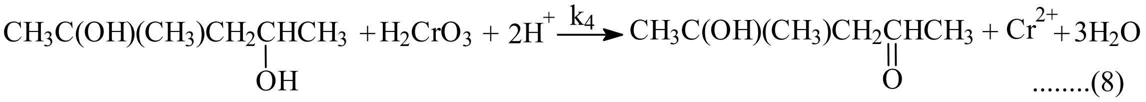
........(5)

$$Cr_2O_7^{2-} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2HCrO_4^{-} \qquad ....(6)$$



$$\underset{\mathbf{P^{+}}}{CH_3C(OH)(CH_3)CH_2}\underset{\substack{|\\ OH_2^{+}}}{C}HCH_3 + HCrO_4^{-} \xrightarrow{k_3} CH_3C(OH)(CH_3)CH_2\underset{\substack{\|\\ O}}{C}HCH_3 + H_2CrO_3 + H_2O$$

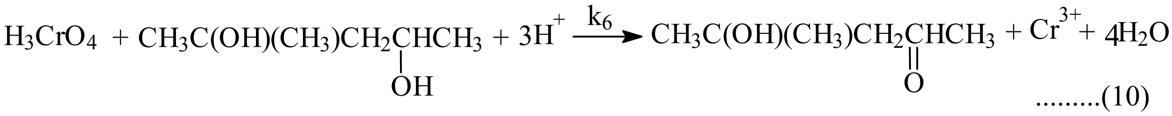
.............(7)



$$CH_3C(OH)(CH_3)CH_2\underset{\substack{|\\ OH}}{C}HCH_3 + H_2CrO_3 + 2H^{+} \xrightarrow{k_4} CH_3C(OH)(CH_3)CH_2\underset{\substack{\|\\ O}}{C}HCH_3 + Cr^{2+} + 3H_2O$$

........(8)

$$Cr^{2+} + HCrO_4^{-} + 2H^{+} \xrightarrow{k_5} Cr^{3+} + H_3CrO_4 \qquad ....(9)$$



$$H_3CrO_4 + CH_3C(OH)(CH_3)CH_2\underset{\substack{|\\ OH}}{C}HCH_3 + 3H^{+} \xrightarrow{k_6} CH_3C(OH)(CH_3)CH_2\underset{\substack{\|\\ O}}{C}HCH_3 + Cr^{3+} + 4H_2O$$

.........(10)

Rate= $k_3[P^+]\,[HCrO_4^-]$ …………………………………………………………(11)
$[P^+] = K_1[P][H^+]$ …………………..………………………………………….. (12)
$\therefore$ Rate = $K_1k_3[P][H^+][HCrO_4^-]$……………………………………………….(13)
where P = pentanediol and P^+ = protonated pentanediol
This is similar to equation (4) where $a = k_1k_3$

Thus, the proposed mechanism is consistent with the results obtained and this has been rationalised on the basis of the following points:

(i) Inhibition of the rate of reaction by the presence of methanoate and ethanoate ions tends to suggest that the reaction occurs through outersphere pathway. Such rationalisation for anion effect on reaction rate has been made for different systems[25, 26, 29,30].

(ii) The absence of gel formation after the addition of methanol and a solution of acrylamide to a partially oxidised mixture shows the absence of a free radical intermediate in the reaction or that the equilibrium constants for the formation of such radical can be assumed to be very small.

(iii) The results of the spectrophotometric measurement displayed no change in λ_{max} from 580 nm when the absorbance of the reaction mixture was monitored one minute after mixing at different wavelengths. Similar observation has been reported to be in support of outersphere pathway.

(iv) A Lineweaver - Burk modification of Michaelis Menten[24,31,32] plot of $1/k_1$ versus 1/[diol] was linear without intercept. This also indicates that intermediate with appreciable equilibrium constants are very unlikely in this reaction.

Convincing arguments that the oxidation of alcohol proceeds through formation of esters of chromic acid have been advanced [2,21]. The co-ordination of reductants to the chromium centre in a step preceding the redox process has been observed in a number of reactions of this oxidant[11] but from (i)-(iv) above, it can be concluded that the spectroscopic and kinetic evidences are not in support of the innersphere mechanism. Therefore we propose outersphere mechanism for this reaction.

Table 1: Rate Constants for the oxidation of 2-methylpentane-2,4-diol by $Na_2Cr_2O_7$ in aqueous HCl at $[Cr_2O_7^{2-}] = 0.01$ mol dm^{-3}, $\lambda_{max} = 580$ nm and T = 27 ± 1 °C

[diol], mol dm^{-3}	$[H^+]$ mol dm^{-3}	I, mol dm^{-3}	10^3 k_2, $dm^3 mol^{-1} s^{-1}$
0.575	0.5	1.0	1.68
0.625	0.5	1.0	1.78
0.700	0.5	1.0	1.68
0.800	0.5	1.0	1.72
0.900	0.5	1.0	1.71
0.625	0.4	1.0	1.32
0.625	0.6	1.0	2.05
0.625	0.7	1.0	2.16
0.625	0.8	1.0	2.69
0.625	0.5	0.60	2.13
0.625	0.5	0.70	2.05
0.625	0.5	0.90	1.89
0.625	0.5	1.10	1.59
0.625	0.5	1.20	1.51

Table 2: Dependence of Second order rate Constant on the added anions for oxidation of 2-methylpentane-2,4-diol by $Cr_2O_7^{2-}$ at $[Cr_2O_7^{2-}] = 0.01$mol dm^{-3}, $\lambda_{max} = 580$ nm and T = 27 ± 1 °C

[diol] mol dm^{-3}	$[H^+]$ mol dm^{-3}	I, mol dm^{-3}	$[HCOO^-]$, mol dm^{-3}	$[CH_3COO^-]$, mol dm^{-3}	10^3 k_2, dm^3 mol^{-1} s^{-1}
0.625	0.5	1.0	0.05	-	1.58
0.625	0.5	1.0	0.10	-	1.45
0.625	0.5	1.0	0.20	-	1.05
0.625	0.5	1.0	0.25	-	0.86
0.625	0.5	1.0	-	0.05	1.49
0.625	0.5	1.0	-	0.10	1.28
0.625	0.5	1.0	-	0.20	0.96
0.625	0.5	1.0	-	0.35	0.47
0.625	0.5	1.0	-	0.45	0.10
0.625	0.5	1.0	-	-	1.10
0.625	0.5	1.0	-	-	1.20
0.625	0.5	1.0	-	-	1.19
0.625	0.5	1.0	-	-	1.25
0.625	0.5	1.0	-	-	1.31
0.625	0.5	1.0	-	-	1.32

REFERENCES

1. Espenson, J. H., **Accounts Chem. Res. 3 (1970) 347.**
2. Westheimer, F. H., **Chem. Rev.45 (1949) 419.**
3. Lee, J. D., **A new Concise Inorganic Chemistry.3rd ed. Van Nostrand Reinhold Co Ltd., U.K. 1983.**
4. Tony, T. Y and King, E. L ., **J. Am.Chem. Soc. 75 (1953) 6180.**
5. Schwarzenbach, G. and Meier, J., **J. Inorg. Nucl. Chem.8 (1958) 302.**
6. Hepler, L .G., **J. Am. Chem. Soc.80 (1958) 6181.**
7. Ukoha, P. O, Agunwa,U. B. and Okonkwo, E. M., **J. Chem. Soc. Nigeria. 26:1 (2001) 81.**
8. Westheimer,F. H., **J. Am. Chem. Soc.74 (1952) 4387.**
9. Kuivila, H.G and Becker,W. J. J., **J. Am. Chem. Soc.74 (1963) 5329.**
10. Wiberg,K. B and Schafer, H., **J. Am.Chem. Soc. 89 (1967) 455.**
11. Olatunji, M. A., **Ph D. Thesis, University of Glassgow, Glassgow. 1975.**
12. Chang, Y .W and Westheimer, F. H., **J. Am.Chem. Soc. 82 (1960) 14.**
13. Haight, G. P, Jursich,G. M., Kelso, M. T. and Merrill, P., **J. Inorg. Chem.24 (1985) 2740.**
14. Chatterji, A. C. and Mukherjee, S. K., **J. Am.Chem. Soc.80 (1958) 3600.**
15. Kemp,T. J. and Walters, W. A., **Proc. Roy. Soc. London.A274 (1963) 480.**
16. Rocek, J and Riehl, A., **Tet. Lett. (1966)1437.**
17. Vogel, I. A., **A Textbook of Quantitative Inorganic Analysis. E.L.B.S and Longman U.K. 1971.**
18. Chatterji, A. C. and Mukherjee, S. K. **Z. Physik Chem., 208 (1958) 281.**
19. Clarke, H. T., **A handbook of Organic Analysis Qualitative and Quantitative,5thed., Edward Arnold Publishers Ltd., London, 1975.**
20. Price, W. J., **The Principle and Practice of Infrared Spectroscopy. 3rd ed. Pye Unicam Ltd, England. 1973.**
21. Westheimer, F and Novick, A**.**, **J. Chem. Phys.11 (1943) 506.**
22. Atkins, P. W. **Physical Chemistry , E.L.B.S, U.K. 1979.**
23. Ayoko, G. A, Iyun, J. F and Okechukwu, R.C., **Bull. Chem. Soc. Ethiopia.4:1 (1990) 33.**
24. Onu, A.D. and Iyun, J.F., **J. Chem. Soc. Nigeria. 26 :2 (2001)156.**
25. Ukoha, P. O and Iyun, J. F., **Nig. J. Chem. Res.4 (1999) 9.**
26. Iyun, J. F., **J. Chem. Soc. Nigeria. 15 (1990) 80.**
27. Lohdip,Y. N., Davies, A. K. and Iyun, J. F., **N. J.T.E,15:2 (1998) 57**.
28. Lohdip,Y. N., **M. Sc. Thesis. Ahmadu Bello University, 1989.**

29. Lohdip,Y. N., **Ph. D. Thesis, Ahmadu Bello University, 1999.**

30. Lohdip, Y. N. and Iyun, J. F., **J. Chem. Soc. Nigeria 18 (1993) 61.**

31. Iyun, J. F, Ayoko, G. A. and Lawal, M .H., **Indian J. Chem.31A (1992) 943.**

32. Michaelis,L. and Menten, M.L., **Biochem. Z. 49 (1939) 33.**

accepted 18/5/05
received 16/2/05