Asian Journal of Chemistry Vol. 3, No. 4 (1991), 385-390

Kinetics and Mechanism of Oxidation of Triphenylarsine by Chromium (VI)

A. CHELLAMANI* AND A. JAWAHAR

Department of Chemistry, VHNSN College, Virudhunagar—626 001 *India*

The Kinetics of oxidation of triphenylarsine by Cr (VI) in 60% acetonitrile–40% water (v/v) mixture to give triphenylarsine oxide follows the rate law,

$$\frac{-d[\mathrm{Cr\ (VI)}]}{dt} = \frac{k\,KK'[\mathrm{Ph_3As}][\mathrm{H_2CrO_4}]_0[\mathrm{H^+}]^2}{K + [\mathrm{H^+}]}$$

The active species involved in the oxidation is $HCrO_3^+$. A mechanism involving a one-electron-transfer process has been proposed.

INTRODUCTION

Although Cr (VI) has been widely used as an oxidant for the oxidation of organic substrates[1], studies with organometallic compounds of Group V elements have not been reported. The present work describes the kinetics and mechanism of the reaction of triphenylarsine (TPA) with Cr (VI) in 60% acetonitrile–40% water (v/v) mlxture.

EXPERIMENTAL

Triphenylarsine (Fluka, AG) was recrystallised from ethanol. Potassium dichromate (BDH, AR) was used as such. A commercial sample of acetonitrile was purified by standard procedure[2]. All theother chemicals used were of AR grade.

The kinetic studies were carried out under pseudo first-order conditions ([TPA] $>>$ [Cr(VI)]) at constant ionic strength (maintained by the addition of sodium perchlorate) by monitoring the disappearance of the ultraviolet absorption characteristics of Cr (VI). $\lambda_{max} = 350$ nm. The pseudo first-order rate constant (k_1) at each kinetic run was evaluated from the slope of linear plot of log (O.D) versus time (correlation coefficient-r > 0.995) by the method of least-squares. The second-order rate constants (k_2) were obtained from $k_2 = k_1/[\mathrm{TPA}]$. The precision of the k values is given in terms of 95% confidence limit of the '*Student t*'.

TLC of the reaction mixture of an actual kinetic run showed the formation of a single product which was identified to be triphenylarsine oxide from UV[3] and IR[4,5] studies ($\bar{\nu}_{\mathrm{As=O}} = 880\ \mathrm{cm^{-1}}$). Estimation of the

---

*Present Address : Department of Chemistry, Madurai Kamaraj University P. G, Extension Centre, Palayamkottai — 627 002, India.

unreacted Cr (VI) from reaction mixtures where [Cr(VI)] > [TPA] after the completion of the reaction showed that three molecules of TPA are oxidised for each two Cr (VI) species reduced to Cr (III). The stoichiometry is represented by

$$3Ph_3As + 2HCrO_3^+ + 4H^+ \rightarrow 3Ph_3AsO + 2Cr^{3+} + 3H_2O \quad ...(1)$$

RESULTS AND DISCUSSION

The reaction is first-order in Cr (VI) as shown by the constant values of the pseudo first-order rate constants at different concentrations of Cr (VI) (Table 1). The concordant values of the second-order rate constants at different concentrations of TPA (Table 1) and the unit slope obtained from the double-logarithmic plot of k_1 and [TPA] (slope = 1.06 ± 0.16, r = 0.995, s = 0·02) indicate that the order with respect to TPA is also one. Further a plote of k_1 versus [TPA] passes through the origin (r = 0.998) showing the second-order nature of the reaction.

TABLE 1

DEPENDENCE OF RATE ON [Cr(VI)] and [TPA]

$10^2[H^+] = 4.0$ mol dm^{-3}, $10^2 \mu = 5.0$ mol dm^{-3}

Solvent = 60% CH_3CN – 40% H_2O (v/v) mixture, temp. = 25°C)

10^4 [Cr(VI)] (mol dm^{-3})	10^3 [TPA] (mol dm^{-3})	10^4k_1[a] (s^{-1})	10^2k_2[a] (dm^3 mol^{-1}s^{-1})
3.00	4.00	4.14±0.18	10.3±0.4
3.50	4.00	4.53±0.13	11.3±0.3
4.00	4.00	4.50±0.16	11.3±0.4
4.50	4.00	4.87±0.18	12.2±0.4
5.00	4.00	4.45±0.19	11.1±0.5
5.50	4.00	4.79±0.17	11.9±0.4
6.00	4.00	4.40±0.17	11.0±0.4
4.00	5.00	5.39±0.15	10.8±0·4
4.00	6.00	7.51±0.24	12.5±0.6
4.00	7.00	8.61±0.33	12.3±0·8
4.00	8.00	9.28±0.24	11.6±0.6
4.00	10.00	11.9±0.2	11.9±0.4
4.00	12.00	14.5±0·2	12.1±0.4

[a] The error quoted in k is the 95% confidence limit of the 'Student t'.

The rate of the reaction increases significantly with increasing [H+] (Table 2). The plot of log k_2 versus log [H+] is found to be linear (slope = 1.56 ± 0.12, r = 0.998, s = 0.02). It shows that the order in $[H^+]$ is fractional {1.56). Variation of the ionic strength of the medium (Table 2) has no effect on the rate. This may presumably due to the participation of neutral species in the rate-determining step. The rate of the reaetion increases with decrease in the water content in the reaction medium (Table 2). A plot of log k_2 versus 1/D is linear with positive slope (r = 0.984, s = 0·06). It is well known according to Amis[6] that reactions which go rapidly with decrease in dielectric constant are all positive ion-dipole reactions. Therefore, in the present investigation the rate-determining step may involve a positive ion and a dipole· A two electron transfer process will result in the formation of Cr (IV), which can be demonstrated by the addition of Mn (II)[7]. The addition will generally lead to a decreased rate of oxidation because Mn (II) removes the Cr (IV) formed. The rate of oxidation of TPA by Cr (VI) is almost unaffected by the addition of Mn (II), ruling out the possibility of the formation of Cr (IV) in the rate-controlling step. Similar observation has been reported for the oxidation of organic sulphur compounds by Cr (VI)[1]. The second-order rate constants at 25, 30, 35, 40 and 45°C are 11.3 ± 0.4, 11.9 ± 0.4, 13.0 ± 0.4, 15.0 ± 0.4 and 17.3 ± 0.9 $dm^3\ mol^{-1}\ s^{-1}$ respectively. The enthalpy and entropy of activation are 14.4 $kJmol^{-1}$ and $-215\ JK^{-1}\ mol^{-1}$ respectively. The reaction is characterised by a low enthalpy of activation and an appreciable negative entropy of activation. The large negative value of the entropy of activation implies that the activated complex should have an exact specificity of orientation.

TABLE 2

EFFECT OF VARYING $[H^+]$, IONIC STRENGTH, AND PERCENTAGE OF SOLVENT COMPOSITION ON THE RATE OF OXIDATION[a]

$10^2[H^+]$ ($mol\ dm^{-3}$)	$10^2k_2{}^b$ ($dm^3\ mol^{-1}s^{-1}$)	$10^2\ \mu$ ($mol\ dm^{-3}$)	$10^2k_2{}^c$ ($dm^3\ mol^{-1}s^{-1}$)	CH_3CN-H_2O (% v/v)	$10^2k_2{}^d$ ($dm^3\ mol^{-1}s^{-1}$)
3.00	6.84 ± 0.06	4.12	10.5 ± 0.4	60 – 40	11.3 ± 0.4
4.00	10.6 ± 0.3	5.00	21.3 ± 0.4	65 – 32	11.7 ± 0.4
5.00	14·6 ± 0.3	6.00	9.99 ± 0.28	70 – 30	15.7 ± 0.7
7.50	26.0 ± 1.0	8.00	10.6 ± 0.3	75 – 25	17.3 ± 1.2
10.0	42.0 ± 0.8	10.0	10.0 ± 0.3	80 – 20	29.5 ± 0.8
12.5	64.3 ± 0.6	14.9	10.8 ± 0.3	85 – 15	42.2 ± 1.2
15.0	87.0 ± 1.2			90 – 10	78.8 ± 1.4

[a] 10^3 [TPA] = 4.0 $mol\ dm^{-3}$, 10^4 [Cr(VI)] = 4.0 $mol\ dm^{-3}$, temp. = 25°C.

[b] 10μ = 1.6 $mol\ dm^{-3}$, Solvent = 60% CH_3CH – 40% H_2O (v/v) mixture.

[c] $10^3\ [H^+]$ = 4.0 $mol\ dm^{-3}$, Solvent = 60% CH_3CN – 40% H_2O (v/v) mixture.

[d] $10^2\ [H^+]$ = 4.0 $mol\ dm^{-3}$, $10^2\mu$ = 5.0 $mol\ dm^{-3}$.

In aqueous solutions of Cr (VI) at concentrations greater than 0.05 mol·dm^{-3}, the dichromate ion and its protonated forms are the predominant species. At dilute solutions (as in the present case) the monomeric form predominates[8]. The acid chromate ion $HCrO_4^-$ does not lose a proton until the pH is raised to about 7 and it gains a second proton in the H_- range of -1 to -3. At higher concentrations of $HClO_4$, Cr (VI) mainly exists as $HCrO_3^+$[7,9] whereas at lower concentrations it exists as $HCrO_4^-$[1,10]. In the present investigation though the acid concentration is low, it is hundred times greater than that of the concentration of Cr (VI). Hence it may be presumed that under the present experimental conditions, Cr (VI) exists largely as $HCrO_3^+$. On the basis of the foregoing arguments based on kinetic data, a mechanism involving a one-electron-transfer process (Scheme 1) may be postulated for the oxidation of TPA by Cr (VI).

$$H_2CrO_4 \overset{K}{\rightleftharpoons} HCrO_4^- + H^+ \qquad \ldots(2)$$

$$HCrO_4^- + 2H^+ \overset{K'}{\rightleftharpoons} HCrO_3^+ + H_2O \qquad \ldots(3)$$

$$Ph_3As + Cr\,(VI) \xrightarrow[\text{slow}]{k} Ph_3\overset{\bullet +}{As} + Cr\,(V) \qquad \ldots(4)$$

$$Ph_3\overset{\bullet +}{As} + Cr\,(V) \longrightarrow Ph_3\overset{+}{As} - O - Cr\,(IV) \qquad \ldots(5)$$

$$Ph_3\overset{+}{As} - O - Cr\,(IV) \xrightarrow{\text{solvolysis}} Ph_3AsO + Cr\,(IV) \qquad \ldots(6)$$

Scheme 1

A similar type of mechanism has been proposed in the reaction of Cr (VI) with organic sulphur compounds[1,12,12]. It is pertinent to mention here that in the oxidation of TPA by hydroperoxides[13], peroxodisulphate[14,15] and peroxodiphosphate[16], polar mechanisms have been suggested. The rate law for the present reaction can be written as

$$-\frac{d[Cr\,(VI)]}{dt} = k[Ph_3As]\,[HCrO_3^+] \qquad \ldots(7)$$

$$\text{i.e.,} \quad -\frac{d[Cr\,(VI)]}{dt} = k\,K'[Ph_3As]\,[HCrO_4^-]\,[H^+]^2 \qquad \ldots(8)$$

From Eq. (2),

$$K = \frac{[HCrO_4^-]\,[H^+]}{[H_2CrO_4]} \qquad \ldots(9)$$

Or

$$K = \frac{[HCrO_4^-][H^+]}{[H_2CrO_4]_0 - [HCrO_4^-]} \qquad \ldots(10)$$

on rearranging Eq. (10),

$$[HCrO_4^-] = \frac{K[H_2CrO_4]_0}{K + [H^+]}$$

Hence Eq. (8) becomes,

$$-\frac{d[Cr\ (VI)]}{dt} = \frac{k\ KK'\ [Ph_3As]\ [H_2CrO_4]_0[H^+]^2}{K + [H^+]} \qquad \ldots(11)$$

Eq. (11) can be rearranged as,

$$\frac{[H]^{+2}}{k_2} = \frac{1}{kK'} + \frac{[H]^+}{kKK'} \qquad \ldots(12)$$

The proposed rate law is consistent with the observed results. The results of H^+ ion dependence can be explained by the rate law (eq. 11). A plot of $[H^+]^2/k_2$ versus $[H^+]$ yields a satisfactory correlation with definite intercept ($r = 0.955$, slope $= 1.16$, intercept $= 1.05 \times 10^{-3}$) and the value of K is calculated to be 9.05×10^{-4}.

ACKNOWLEDGEMENT

The authors are grateful to Prof. C. Srinivasan for helpful discussions.

REFERENCES

1. C. Srinivasan, A. Chellamani and S. Rajagopal, *J. Org, Chem.*, **50**, 1201 (1985), and references cited therein.
2. J. F. Coetzee, *Progr. Phys. Org. Chem.*, **4**, 45 (1967).
3. H. H. Jaffe, *J. Chem. Phys.*, **22**, 1430 (1954).
4. D. J. Phillips and S. Y. Tyree Jr., *J. Am. Chem. Soc.*, **83**, 1806 (1961).
5. D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 2298 (1961).
6. E. S. Amis, Solvent Effects on Reaction Rates and Mechanism, Academic Press, New York pp. 42, 43 (1966).
7. G. T. E. Graham and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 3030 (1958).
8. K. B. Wiberg, Oxidation in Organic Chemistry, Academic Press, New York, pp. 71, 182 (1965).
9. L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).
10. K. B. Wiberg and T. Mill *J. Am. Chem. Soc.*, **80**, 3022 (1958).
11. V. Baliah and P. V. V. Satyanarayana, *Indian J. Chem.*, **16A**, 966 (1978),
12. C. Srinivasan, R. Venkatasamy and S. Rajagopal, *Indian J. Chem.* **20A**, 505 (1981).

13. R. Hiatt, C. McColeman and G. R. Howe, *Can. J. Chem.*, **53**, 559 (1975).
14. C. Srinivasan and K. Pitchumani, *Int. J. Chem. Kinet.*, **14** 1315 (1982).
15. C. Srinivasan and A, Chellamani, *Indian J. Chem.*, **23A**, 684 (1984).
16. C. Srinivasan and K. Pitchumani, *Can. J. Chem.*, **63**, 2285 (1985).

[*Received* : 1 December, 1989; *Accepted* : 5 July 1990) AJC–203