Asian Journal of Chemistry Vol. 12, No. 4 (2000), 967–972

Kinetics and Mechanistic Studies of Oxidation of V(IV) by ICl and IBr in Aqueous Acetic Acid and Perchloric Acid Medium

P.S. RADHAKRISHNA MURTI, KIRAN S. TRIPATHY* and EJAZ AHMED
Department of Chemistry, Berhampur University, Berhampur-760 007, India

A kinetic study on the oxidation of V(IV) by iodine monochloride (ICl) and iodine monobromide (IBr) in aqueous acetic acid and perchloric acid media has been carried out. In both the systems studied the order with respect to oxidant is unity. In case of ICl the dependence on [substrate] is fractional whereas in [IBr] it is unity. The order with respect to $[H^+]$ in ICl and IBr reactions is inverse fractional. The rate of reaction remains invariant to the change in composition of a complex between the hydrolysed species of V(IV) and the effective species of the oxidant in a reversible equilibrium.

INTRODUCTION

Electron transfer reactions between V(IV) and Cr(VI)[1], Mn(III)[2] and Br(V)[3] have been reported. Subsequently in our laboratory, the oxidation of V(VI) by uncatalysed chloramine-T (CAT), N-bromo-succinamide (NBS), N-iodo-succinamide (NIS)[4] and I(V)[5] catalysed by Os(VIII) and Ru(III) and molecular iodine[6] has been studied. A symmetric study of V(IV) by ICl and IBr in acetic and perchloric acids has been made. A survey of literature indicates that there is no kinetic report having these oxidants.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. The kinetics of reaction has been followed by estimating the unreacted oxidants in each case iodometrically towards a starch-iodine end point against standard thiosulphate. The rate constants are reproducible within ±3%.

RESULTS AND DISCUSSION

Oxidation by IBr: The reaction shows unit dependence with respect to oxidation and substrates (Table-1). The dependence on $[H^+]$ is inverse fractional (Table-1). Increase in percentage of the solvent has a marginal acceleration as observed. The various activation parameters are $\Delta E^{\neq} = 95.8$ kJ mole^{-1}, $\Delta H^{\neq} = 92.9$ kJ mole^{-1}, $\log_{10} A = 12.7$ and $\Delta S^{\neq} = -12.14$ J K^{-1} mole^{-1}.

TABLE-1
PSEUDO-FIRST-ORDER CONSTANTS AT CARRYING [IBr], [V(IV)] AND $HClO_4$

Solvent = 10%(v/v), aq. Acetic acid, $[Hg(OAc)_2] = 0.001$ M, Temp. = 60°C

$10^4 \times$ [IBr] M	$10^3 \times$ [V(IV)] M	$10^2 \times [H^+]$ M	$10^3 \times k_1$ min
2.5	5.0	2	1.30
5.0	5.0	2	1.32
7.6	5.0	2	1.30
10.0	5.0	2	1.29
5.0	2.5	2	0.65
5.0	10.0	2	2.66
5.0	15.0	2	3.76
5.0	5.0	1	2.04
5.0	5.0	3	1.01
5.0	5.0	4	0.85
5.0	5.0	2	1.60^{a1}
5.0	5.0	2	1.96^{a2}
5.0	5.0	2	3.60^{b1}
5.0	5.0	2	7.98^{b2}

a1 & a2: at HOAc 20 and 30% (v/v)
b1 & b2: at temp. 70 and 80°C

Mechanism

According to Millitzer,[7] IBr polarises into I^- and Br^+. This suggestion has been criticised by Bennett and Sharpe[8] as the polarisation of IBr into I^- and Br^+ is contrary to the greater electron-positive character of iodine than that of bromine. They proposed that bromine arising by thermal dissociation of IBr is the actual brominating agent. But in the present investigation due to the presence of $Hg(OAc)_2Br_2$ as a species, this is unlikely. Hence it is concluded that IBr functions as a neutral molecule. V(IV) complexes with the neutral molecule in a rate determining step to give the product:

$$VO^{2+} + H_2O \xrightleftharpoons{K_h} VOOH^+ + H^+$$

$$\begin{tikzcd} VOOH^+ + IBr \arrow[r, shift left, "k_1"] & {[VOOH^+ \ldots IBr]} \arrow[l, shift left, "k_{-1}"] \\ & {[\text{Complex}]} \arrow[d, "k"', "\text{slow}"] \\ & VO_2 + H^+ + I^- Br^+ \end{tikzcd}$$

Scheme-I

Rate Law:

$$\text{Rate} = -\frac{k[\text{complex}]}{dt} = k[\text{complex}]$$

Applying steady state treatment to the complex,

$$k_1[\text{VOOH}^+][\text{Br}] = (k_{-1} + k)[\text{complex}]$$

$$[\text{complex}] = \frac{k_1[\text{VOOH}^+][\text{Br}]}{(k_{-1} + k)}$$

$$= \frac{k_1[\text{VOOH}^+][\text{Br}]}{(k_{-1} + k)[\text{H}^+]}$$

$$[\text{VO}^{2+}]_T = [\text{VO}^{2+}] + [\text{VOOH}^+]$$

$$= [\text{VO}^{2+}]\left\{1 + \frac{K_h}{[\text{H}^+]}\right\}$$

$$[\text{VO}^{2+}] = \frac{[\text{VO}^{2+}]_T[\text{H}^+]}{K_h + [\text{H}^+]}$$

$$[\text{Complex}] = \frac{k_1[\text{VO}^{2+}]_T[\text{IBr}]}{(k_{-1} + k)(K_h + [\text{H}^+])}$$

$$\text{Rate} = \frac{k[\text{complex}]}{dt} = k[\text{complex}]$$

$$= \frac{kk_1[\text{VO}^{2+}]_T[\text{IBr}]}{(k_{-1} + k)(K_h + [\text{H}^+])}$$

This explains all the observed kinetic orders.

Oxidation by ICl: The reaction exhibited first order in oxidation as revealed by the linear plots of log (a – x) *vs.* time (Table-2). The plot of log k_1 *vs.* log [s] (Fig. 1) is linear with a slope less than unity confirming fractional order dependence of substrate. Further, the double reciprocal plot of $1/k_1$ versus 1/[s] (Fig. 2) is linear with a finite intercept on the inverse rate axis indicating complex formation between the substrates and the oxidant. The reaction has inverse fractional dependence on acidity (Table-3). the plot of log k_1 *vs.* log $[\text{H}^+]$ is linear with a negative slope less than unity. It has been reported earlier by Selbin[9] that V(IV) in aqueous acid medium $\{[\text{H}^+] = 0.002\text{–}3\ \text{M}\}$ hydrolyses to VOOH^+ with an approximate k_h value of 10^{-6}. The active species of the substrate participating in the reaction is VOOH^+, and hence the inverse dependence on acidity. The effect of solvent is marginal. The values of activation parameters at 60°C have been found to be $\Delta E^{\neq} = 95.75\ \text{kJ mole}^{-1}$, $\Delta H^{\neq} = 93\ \text{kJ mole}^{-1}$, $\log_{10} A = 13.46$ and $\Delta s^{\neq} = -0.8\ \text{J K}^{-1}\ \text{mole}^{-1}$.

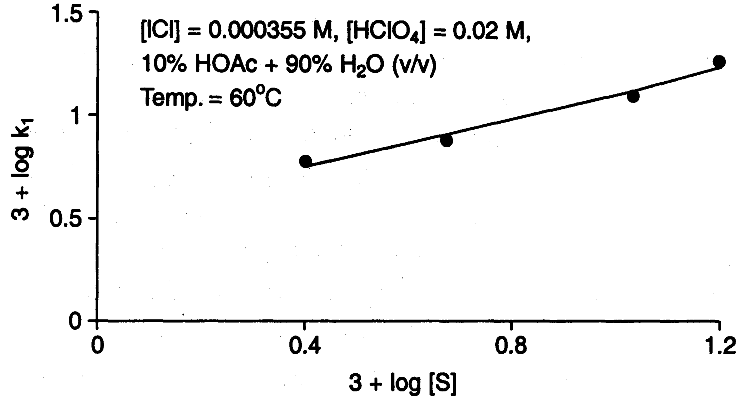

Fig. 1 log k_1 *vs.* log [S]

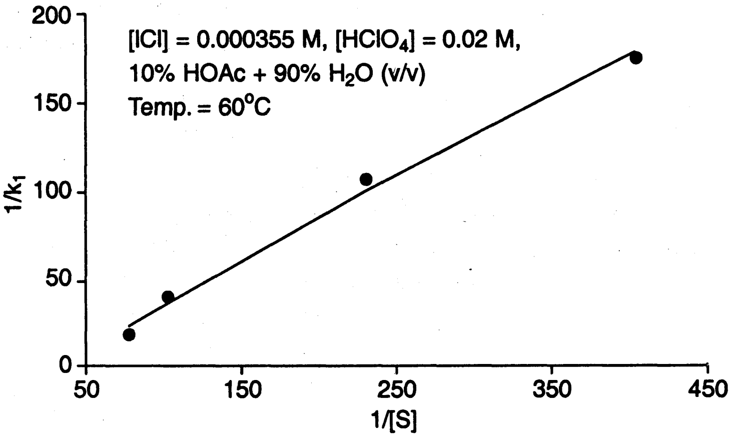

Fig. 2 $1/k_1$ *vs.* 1/[S]

Mechanism

In pure water ICl is hydrolysed to HCl and HOI and the latter then changes into iodic acid with separation of iodine. The hydrolysis is favoured only at [H^+] below [0.2 M]. Under the experimental conditions of [H^+] = [0.02 M] the hydrolysis yielding HOI or H_2OI^+ is favoured. The other species like ionic species I^+ and Cl^- are also not favoured as the former is not formed and the latter if formed is inert. Further ICl_2^- demands a nucleophilic attack, which is forbidden. So in the present study it appears that it is the neutral molecule alone that complexs with $VOOH^+$, which further breaks down with a one electron transfer leading to I^- which subsequently reacts with another V(IV) in a fast step giving the products.

TABLE-2
PSEUDO-FIRST-ORDER CONSTANTS AT CARRYING [ICl], [V(IV)] AND $HClO_4$

Solvent = 10%(v/v), aq. Acetic acid, Temp. = 60°C

$10^4 \times$ [ICl] M	$10^3 \times$ [V(IV)] M	$10^2 \times [H^+]$ M	$10^3 \times k_1$ min
1.80	5.0	2	8.70
3.55	5.0	2	8.50
5.40	5.0	2	8.24
7.25	5.0	2	8.10
3.55	2.5	2	5.70
3.55	10.0	2	12.80
3.55	15.0	2	18.90
3.55	5.0	1	11.36
3.55	5.0	3	6.82
3.55	5.0	4	5.68
3.55	5.0	2	7.86[a1]
3.55	5.0	2	7.30[a2]
3.55	5.0	2	3.52[b1]
3.55	5.0	2	25.55[b2]

a1 & a2: at HOAc 20 and 30% (v/v)
b1 & b2: at temp. 50 and 70°C

$$VO^{2+} + H_2O \overset{K_h}{\rightleftharpoons} VOOH^+ + H^+$$

$$\begin{array}{l} VOOH^+ + ICl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [VOOH^+ \ldots ICl] \\ \qquad\qquad\qquad\qquad\qquad [\text{Complex}] \\ \qquad\qquad\qquad\qquad\qquad\quad k_2 \big\downarrow \text{slow} \\ \qquad\qquad\qquad\qquad\qquad VO_2^{2+} + HCl + I^- \end{array}$$

$$VO^{2+} + H_2O \xrightarrow{\text{fast}} VO_2 + 2H^+ + I^-$$

Scheme-II

Rate Law:

$$[VOOH^+] = \frac{K_h[VO^{2+}]}{[H^+]}$$

Applying steady state treatment to the complex,

$$k_1[VOOH^+][ICl] = (k_{-1} + k_2)[\text{complex}]$$

$$[\text{complex}] = \frac{k_1[\text{VOOH}^+][\text{ICl}]}{(k_{-1} + k_2)}$$

$$[\text{ICl}]_T = [\text{ICl}] + [\text{Complex}]$$

$$= [\text{ICl}]\left\{1 + \frac{k_1[\text{VOOH}^+]}{(k_{-1} + k_2)}\right\}$$

$$[\text{ICl}] = \frac{(k_{-1} + k_2)[\text{ICl}]_T}{k_{-1} + k_2 + k_1[\text{VOOH}^+]}$$

$$[\text{Complex}] = \frac{k_1[\text{VOOH}^+][\text{ICl}]_T}{k_{-1} + k_2 + k_1[\text{VOOH}^+]}$$

$$= \frac{k_1K_h[\text{VO}^{2+}][\text{ICl}]_T}{[\text{H}^+]\{k_{-1} + k_2 + k_1K_h[\text{VO}^{2+}]/[\text{H}^+]\}}$$

$$= \frac{k_1K_h[\text{VO}^{2+}][\text{ICl}]_T}{(k_{-1} + k_2)[\text{H}^+] + k_1K_h[\text{VO}^{2+}]}$$

$$\text{Rate} = \frac{d[\text{ICl}]}{dt}$$

$$= \frac{d[\text{complex}]}{dt}$$

$$= k_2[\text{Complex}]$$

$$= \frac{k_1k_2K_h[\text{VO}^{2+}][\text{ICl}]_T}{(k_{-1} + k_2)[\text{H}^+] + k_1K_h + [\text{VO}^{2+}]}$$

which explains all the observed kinetic orders.

Conclusion

It has been established that V(IV) reactions are routed through VOOH^+ in all the oxidations studied, whereas the reaction with ICl and IBr and VOOH^+ is followed by slow decomposition of the complex. These are the essential conclusions reached.

REFERENCES

1. Espenson, *J. Am. Chem. Soc.*, **86,** 1983 (1964).
2. Rosseinsky and Nicol, *J. Am. Chem. Soc.*, **90,** 1022 (1968).
3. Thomson, *J. Am. Chem. Soc.*, **93,** 7315 (1971).
4. N.C. Sahu, Ph.D. Thesis, Berhampur University (1982).
5. Gillford and Ottaway, *Analyser*, **97,** 412 (1972).
6. P.S. Radhakrishna Murti and S. Misra, *Int. J. Chem. Kinet.*, **14,** 631 (1982).
7. Millitzer Walter, *J. Am. Chem. Soc.*, **60,** 256 (1938).
8. Bennett and Shape, *J. Chem. Soc.*, 1383 (1950).

(*Received:* 17 January 2000; *Accepted:* 18 May 2000) AJC-2038