

Kinetics of Oxidation of Hypophosphorous Acid by Hexachloroiridate(IV) in Perchloric Acid Medium

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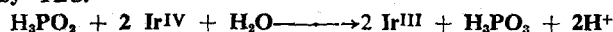
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Hypophosphorous acid reacts with hexachloroiridate(IV) in aqueous perchloric acid solution to give phosphorous acid, detected by TLC.



The total order of the reaction is two; being unity in each reactant, Ir(IV) and H_3PO_2 . The addition of different salts (sodium chloride and sodium sulphate) accelerates the rate of reaction. Added dioxane has insignificant effect on the rate. Hypophosphorous acid reacts with hexachloroiridate(IV) to give free radicals and hexachloroiridate(III). The free radicals further pick up another hexachloroiridate(IV) and by fast steps give the reaction products.

THE oxidation of hypophosphorous acid, using a number of oxidants has been studied¹⁻⁵. The kinetics of oxidation of hypophosphorous acid by Ir(IV) has not received any attention. In another paper⁶, we have shown that hexachloroiridate(IV) acts as a one equivalent oxidant in the oxidation of hydroxylammonium ion. In this paper we present the results of kinetic investigation of the oxidation of hypophosphorous acid by hexachloroiridate(IV).

Materials and Methods

Hypophosphorous acid (Riedel, Germany) used was at least 99% pure. Its solution was standardized iodometrically. The solution of sodium hexachloroiridate, $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (Johnson-Mathey) was prepared in perchloric acid and standardized spectrophotometrically⁷. The other chemicals were of GR grade (E. Merck). All solutions were made in doubly distilled water. Dioxane was purified by distilling twice over metallic sodium, each time collecting the middle fraction. All glass vessels were either Corning or Pyrex.

Kinetic measurement — The rate of reaction was followed by measuring the decrease in Ir(IV) concentration spectrophotometrically at 488 nm⁸. The reactions were studied in the thermostated cell compartment of a Hilger (UVISPEK) spectrophotometer, the temperature being controlled within $\pm 0.1^\circ\text{C}$. The other products were transparent at this wavelength. The reactants were equilibrated separately, mixed externally and then immediately transferred into a cell of path length 1 cm. The rate of decrease of Ir(IV) was followed for two half lives for most of the runs. The pseudo-first order rate constants (k_{obs}) were obtained graphically from the plots of $\log A$ (A = absorbance) against time. The rate constants were reproducible within $\pm 5\%$.

Polymerization test — The reaction between hypophosphorous acid and hexachloroiridate (IV) was studied in 40% (w/v) solution of acrylamide. Substrate (1 ml, 0.4 M) was added to a mixture containing $1 \times 10^{-4} \text{M}$ Ir(IV) (2ml) and acrylamide (3 ml). The acidity and the total volume was adjusted to 0.50 M and 10 ml respectively. The addition of methanol to the reaction mixture led to the formation of white suspension. Control experiments from which either substrate or Ir(IV) were excluded gave no detectable evidence of polymer formation in methanol.

Stoichiometry and products — Hypophosphorous acid under the present experimental condition reacted with Ir(IV) according to Eq. (1).



Phosphorous acid was identified⁹ by TLC (R_f value = 0.75, lit¹⁰ R_f value = 0.75). A control TLC experiment with a mixture of hypophosphite, phosphite and phosphate together with one in which phosphite was reacted with hexachloroiridate(IV) in the acid medium indicated that phosphorous acid is not oxidized by Ir (IV) to phosphoric acid stage. Again, it was found that more than 90% of IrCl_6^{3-} underwent aquation¹¹ to $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ after 5 hrs although no significant aquation ($< 5\%$) of IrCl_6^{3-} had taken place during the kinetic experiment.

Results

Effect of varying reactant concentrations — The reaction was studied at varying concentrations of Ir(IV) in the range $(0.8 \text{ to } 4.8) \times 10^{-4} \text{M}$ at $[\text{H}_3\text{PO}_2] = 4 \times 10^{-1} \text{M}$, $[\text{H}^+] = 1.26 \text{M}$ and 23°C , and the pseudo-first order rate constant was found to be

$(2.06 \pm .03) \times 10^{-4}$ (sec^{-1}). The order in H_3PO_2 is also essentially one as can be seen from the data in Table 1.

Effect of varying Ir(III) concentration — The effect of addition of Ir(III) was studied at $[\text{Ir(IV)}]$, $[\text{H}_3\text{PO}_2]$, $[\text{H}^+]$ and temperature of $1.0 \times 10^{-4}M$, $4.0 \times 10^{-1}M$, $1.26M$ and 35.5°C respectively. The pseudo-first order rate constants at $[\text{Ir(III)}]$ of 0 , 1×10^{-4} , 1.5×10^{-4} , 2×10^{-4} and $5 \times 10^{-4}M$ are 5.05×10^{-4} , 5×10^{-4} , 4.95×10^{-4} , 5×10^{-4} and 5.1×10^{-4} (sec^{-1}) respectively, indicating that Ir(III) does not inhibit the rate of oxidation of H_3PO_2 .

Effect of varying pH — The effect of acidity (varied by the addition of perchloric acid) was studied at $[\text{Ir(IV)}] = 8 \times 10^{-5}M$, $[\text{H}_3\text{PO}_2] = 1 \times 10^{-1}M$ and ionic strength = $1.0 M$. The rate is independent of $[\text{H}^+]$ in the range 0.2 to $1.0 M$.

Effect of added salts — The effect of addition of salts like sodium perchlorate, sodium chloride and sodium sulphate on the pseudo-first order rate constants was studied. Unlike sodium perchlorate the increases in pseudo-first order rate constants are significant in both sodium chloride and sodium sulphate (Table 2) in the concentration range studied.

Effect of solvent — The effect of changing dielectric constant of the medium on the pseudo-first order rate constant was studied by the addition of dioxane. The addition of dioxane to the reaction mixture

increases the rate constant by about 15% when added to the extent of 20% (v/v) and thereafter added dioxane has no significant effect on the pseudo-first order rate constant (Table 3). The result is expected if one assumes the reaction between an ion and uncharged molecule.

Effect of varying temperature — The values of k ($k = k_{\text{obs}}/[\text{substrate}]$) were found to be 5.05×10^{-4} , 6.63×10^{-4} , 11.1×10^{-4} and 22.6×10^{-4} ($\text{litre mol}^{-1} \text{sec}^{-1}$) at 25° , 29.7° , 34.7° and 39.8°C respectively. The value of energy of activation (E_a) was calculated from the linear plot of $\log k$ against $1/T$ by the method of least square and the entropy of activation

was then calculated from the relation, $PZ = e \left(\frac{kT}{h} \right)$.

$\exp \left(\frac{\Delta S^\ddagger}{R} \right)$. The values of E_a and ΔS^\ddagger are 78.8

kJ mol^{-1} and $-53.2 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. The energy and entropy values are not highly different than the values found for a bimolecular reaction¹¹ between an ion and a neutral molecule.

Discussion

Hypophosphorous acid which ionizes to H^+ and H_2PO_2^- has a dissociation constant^{6a} of 1×10^{-1} at 25°C . The reaction may, therefore, take place between Ir(IV) and hypophosphorous acid or its anion as shown in Scheme 1.

If the reactive species were only H_2PO_2^- , the rate expression, would have involved a complex func-

TABLE 1 — EFFECT OF VARYING SUBSTRATE CONCENTRATION AT DIFFERENT TEMPERATURES

$[\text{Ir(IV)}] = 1.35 \times 10^{-4}M$; $[\text{H}^+] = 1.26 M$

$[\text{H}_3\text{PO}_2]$ M	$k_{\text{obs}} \times 10^4$ (sec^{-1})	$k_{\text{obs}}/[\text{H}_3\text{PO}_2] \times 10^4$ ($\text{litre mol}^{-1} \text{sec}^{-1}$)
TEMP. = 25°C		
0.2	1.25	6.25
0.4	2.30	5.75
0.8	3.84	4.79
1.2	5.76	4.79
1.6	7.40	4.62
2.0	9.21	4.60
2.6	11.89	4.57
TEMP. = 29.7°C		
0.2	1.47	7.35
0.4	2.67	6.67
0.8	5.18	6.47
1.2	7.67	6.39
1.6	10.03	6.27
TEMP. = 34.7°C		
0.2	2.42	12.1
0.4	4.37	10.9
0.8	8.68	10.8
1.2	13.0	10.8
1.6	17.3	10.7
TEMP. = 39.8°C		
0.2	4.73	23.6
0.4	9.40	23.5
0.8	18.6	23.3
1.2	25.5	21.3
1.6	33.8	21.1

TABLE 2 — EFFECT OF ADDED SALT ON THE PSEUDO-FIRST ORDER RATE CONSTANT

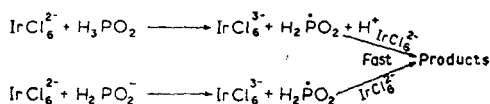
$[\text{Ir(IV)}] = 1.30 \times 10^{-4}M$; $[\text{H}_3\text{PO}_2] = 4.0 \times 10^{-1}M$; $[\text{H}^+] = 1.26 M$; TEMP. = 30°C

$[\text{Salt}]$ M	$k_{\text{obs}} \times 10^4$ (sec^{-1})	
	NaCl	Na_2SO_4
0	2.80	2.80
0.1	3.45	—
0.2	3.88	3.55
0.3	4.73	3.88
0.4	5.18	4.26
0.5	6.50	5.73

TABLE 3 — EFFECT OF SOLVENT ON PSEUDO-FIRST ORDER RATE CONSTANT

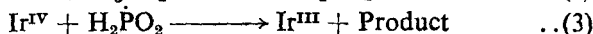
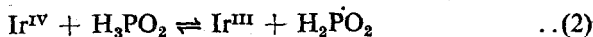
$[\text{Ir(IV)}] = 1.23 \times 10^{-4} M$; $[\text{H}_3\text{PO}_2] = 4.0 \times 10^{-1}M$; $[\text{H}^+] = 1.26 M$; TEMP. = 30°C

Dioxane (%, v/v)	Dielectric constant	k_{obs} (sec^{-1})
0	76.73	2.80
10	67.98	2.94
20	59.24	3.30
30	50.54	3.19
40	41.80	3.26



Scheme-1

tion of $[\text{H}^+]$. Since most of the experiments have been conducted at $[\text{H}^+] = 1.26 \text{ M}$, it is presumed that the main reaction takes place between undissociated hypophosphorous acid and Ir(IV). The results presented in Table 3 indicate that the reaction takes place between an ion and an uncharged molecule. Hexachloroiridate(IV) is known to be stable^{12,13} towards substitution or hydrolysis over wide range of acidities. The photochemical behaviour of IrCl_6^{2-} was investigated in acid solution by Moggi *et al.*¹⁴ who showed that the complex was a little photo-sensitive. Irradiation with 254 nm, no post photochemical effect was observed. Consequently, photochemically induced reactions^{15,16}, are not expected under the present reaction conditions. It is, therefore, suggested that hexachloroiridate (IV) oxidizes hypophosphorous acid initially to give free radicals. This is supported by the formation of suspension on adding acrylamide to the reaction mixture. Again, since Ir(III) does not inhibit the rate of reaction, oxidation of hypophosphorous acid by steps (2) and (3) may not take place.



The electron transfer from substrate to hexachloroiridate(IV) leading to the formation of phosphorous acid may be explained by either of the following schemes (2 and 3).

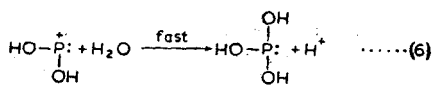
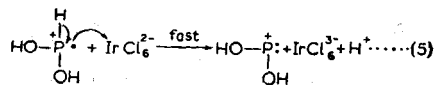
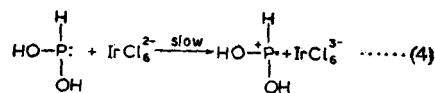
Littler and coworkers¹⁷ have shown that aquopentachloroiridate(III) is generated during the oxidation of some organic compounds by hexachloroiridate(IV). Since hexachloroiridate(IV) is inert towards substitution and phosphorous acid is obtained as one of the reaction products, the formation of $\text{IrCl}_5(\text{OH}_2)^{2-}$ is unlikely. Consequently, hexachloroiridate(IV) is reduced mainly to hexachloroiridate (III) in the present study.

Acknowledgement

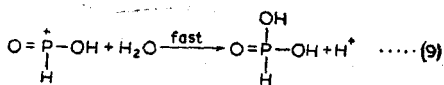
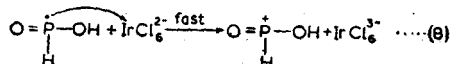
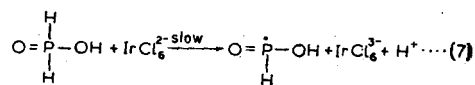
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Scheme-2



Scheme-3

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