

Kinetics and Mechanism of Electron-transfer Reactions of Bismuth(v) in Aqueous Acidic Perchlorate-Fluoride Media. Part 1. Oxidation of Hypophosphorous Acid

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Solutions of bismuth(v) from NaBiO_3 have been obtained in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ and $1.5 \text{ mol dm}^{-3} \text{ HF}$ with a view to studying the redox system involving Bi^{V} and H_3PO_2 . The reaction is first order in the concentration of each of Bi^{V} , H_3PO_2 , and H^+ . It is catalysed by Bi^{III} through complex formation with the reactive species HBiF_6 . The rate law (i) holds where K_p is the protonation

$$-\frac{d[\text{Bi}^{\text{V}}]}{dt} = \left(K_p k' + \frac{K_p K k [\text{Bi}^{\text{III}}]}{1 + K [\text{Bi}^{\text{III}}]} \right) [\text{Bi}^{\text{V}}] [\text{H}_3\text{PO}_2] [\text{H}^+] \quad (\text{i})$$

constant of $[\text{BiF}_6]^-$ and K the complex formation constant between Bi^{V} and Bi^{III} . The values of $K_p k$ and K were found to be $0.125 \pm 0.015 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ and $45 \pm 6 \text{ dm}^3 \text{ mol}^{-1}$ respectively at 35°C and $I = 2.0 \text{ mol dm}^{-3}$; k' and k are the second-order rate constants for the reaction between HBiF_6 and H_3PO_2 , and the complex and H_3PO_2 respectively. Bismuth(v) does not absorb in the u.v. region but Bi^{III} does, the wavelength depending on the source of Bi^{III} and the medium.

Little is known about the solution chemistry of bismuth(v) and much less about its redox kinetics. Fluorine compounds¹ and oxides² of bismuth(v) are known, and sodium bismuthate (NaBiO_3) is commercially available. However, the inability to obtain bismuth(v) in solution from bismuthate has been a great handicap in the study of its solution properties. The first successful attempt seems to have been made by Burstein and Wright³ who obtained fluoride complexes of Bi^{V} in a mixture of $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ and $1.52 \text{ mol dm}^{-3} \text{ HF}$. Another paper⁴ reported very dilute solutions (*ca.* $10^{-4} \text{ mol dm}^{-3}$) of Bi^{V} in aqueous HClO_4 .

The use of sodium bismuthate in the solid state as a strong oxidant is well known in analytical chemistry⁵ and synthetic organic chemistry.⁶ In addition, the selective oxidation of urinary corticosteroids is much applied in chromatographic analysis.⁷ There is only one report^{4,8} on the kinetics of the oxidation of halides, thiocyanate, Ti^{I} , and hexachloroiridate with bismuth(v). The rate is independent of the reductant and formation of Bi^{IV} and OH is considered to be rate controlling.

Our primary aim in investigating bismuth(v) is to determine the mechanism of its reduction and the relevant solution chemistry. The present communication reports the results of its oxidation of hypophosphorous acid.

Experimental

Materials.—Sodium bismuthate (AR Riedel) was the source of bismuth(v). Sodium dihydrogenhypophosphite (NaH_2PO_2) was E. Merck GR quality. Bismuth(III) nitrate and Bi_2O_3 (BDH AnalaR) were used as sources of Bi^{III} . Perchloric acid and hydrofluoric acid were Riedel AR quality. Sodium dihydrogenphosphite was from Riedel. Corning glass vessels were employed for the reactions and storing the solutions, Teflon vessels for storing bismuth(v) solutions in a mixture of HClO_4 and HF.

Bismuth(v) solution. The requisite quantity of sodium bismuthate was digested³ in a mixture of $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ and $1.5 \text{ mol dm}^{-3} \text{ HF}$ to give a clear solution after 10–15 min with some white solid. The solution was decanted and standardized iodometrically⁹ (see later). It is fairly stable for 2 h particularly at low temperature (5°C). Fresh solutions of Bi^{V}

were prepared when required. No hydrogen peroxide could be detected in such solutions at any stage. However, they contained large quantities of Bi^{III} , present either as an impurity in the bismuthate sample and/or formed during the process of digestion by the reduction of Bi^{V} and oxidation of water to oxygen. It was not possible³ to prepare solutions of Bi^{V} free from Bi^{III} ; such solutions always contained about 35% Bi^{III} .

We tried to prepare aqueous solutions⁴ of Bi^{V} in HClO_4 by shaking NaBiO_3 with $5.0 \text{ mol dm}^{-3} \text{ HClO}_4$ for several hours and then centrifuging, but no Bi^{V} was obtained in solution (tested iodometrically). However, it is possible to obtain a fine suspension which slowly disappears through its reaction with water: 0.5 g of NaBiO_3 in $5.0 \text{ mol dm}^{-3} \text{ HClO}_4$ (10 cm^3) disappears in about 24 h with no oxidant present in the solution (tested iodometrically).

Kinetic Procedure.—Reactions were carried out in a thermostatic water-bath at $(35 \pm 0.1)^\circ \text{C}$ unless otherwise stated. The measured quantities of Bi^{V} and other components were mixed and kept in the water-bath to attain the desired temperature. The reaction was initiated by adding corresponding equilibrated hypophosphite solution. The order of mixing of the reactants had no effect on the rate. Aliquots (5 or 10 cm^3) were analyzed iodometrically⁹ for Bi^{V} after suitable intervals of time. There was no photochemical effect.

Initial rates were calculated by the plane-mirror method.¹⁰ Pseudo-first-order plots were employed for reactions with at least a ten-fold excess of hypophosphite, second-order plots when the concentrations of the two reactants were comparable. The second-order rate constants calculated from the two types of plot were similar and reproducible to $\pm 10\%$.

Since the bismuth(v) solutions were not free from bismuth(III) and the rate of reaction increases in the presence of the latter, all kinetic runs were carried out in the presence of a known excess of Bi^{III} prepared from $\text{Bi}(\text{NO}_3)_3$ or Bi_2O_3 .

Iodometric Determination of Bi^{V} .—Aliquots of the reaction mixture or known volumes of the test solution were mixed with $0.01 \text{ mol dm}^{-3} \text{ KI}$ (*ca.* 10 cm^3). The mixture was adjusted to pH 2–3 by adding suitable amounts of NaOH (indicated by the appearance of a slight turbidity). Then 0.01 mol dm^{-3}

ethylenediaminetetra-acetate (edta) (5 cm^3) was added to complex Bi^{III} and the liberated iodine was titrated against a standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ using starch as an indicator. The end-point is sharp only when the pH lies between 2 and 3.

Spectrophotometry.—U.v. measurements were made on solutions of Bi^{V} in aqueous ($\text{HClO}_4 + \text{HF}$) and of Bi^{III} in aqueous HClO_4 . Although it was not possible to obtain Bi^{V} free from Bi^{III} , the former does not appear to absorb in the u.v. region. There were three different sources of Bi^{III} , viz. $\text{Bi}(\text{NO}_3)_3$, Bi_2O_3 , and sodium bismuthate (Bi^{III} being present as an impurity). Aqueous solutions of $\text{Bi}(\text{NO}_3)_3$ absorb at 200 nm ($\epsilon = 4.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ solutions of $\text{Bi}(\text{NO}_3)_3$ absorb at 200–204 nm [$\epsilon = (2.7 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 202 nm], Bi^{III} from Bi_2O_3 in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ absorbs at 222 nm ($\epsilon = 1.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) as also reported earlier,³ and Bi^{III} obtained by shaking solid NaBiO_3 in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ absorbs at 222 nm ($\epsilon = 1.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). It is obvious that the species of Bi^{III} obtained from NaBiO_3 is similar to that obtained from Bi_2O_3 , and that it may be a oxohydroxy-species, $\text{BiO}(\text{OH})$. The nitrate salt $\text{Bi}(\text{NO}_3)_3$ absorbs at lower wavelength since the species formed is different, perhaps $\text{BiO}(\text{NO}_3)$. Such a spectral shift¹¹ on replacing OH by NO_3 is expected.

Table 1. Initial rates (v_0), pseudo-first-order rate constants (k_1), and second-order rate constant (k_2) in the $\text{Bi}^{\text{V}} + \text{H}_3\text{PO}_2$ reaction at 35°C , $[\text{HClO}_4] = 1.0$, $[\text{HF}] = 1.5$, and $[\text{Bi}^{\text{III}}] = 0.01 \text{ mol dm}^{-3}$

$10^3[\text{Bi}^{\text{V}}]$ mol dm^{-3}	$10^3[\text{H}_3\text{PO}_2]$ mol dm^{-3}	$10^7 v_0$ mol $\text{dm}^{-3} \text{ s}^{-1}$	$10^4 k_1$ s^{-1}	$10^2 k_2^*$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0.88	10.0	3.75		4.20
1.76	10.0	7.3		4.10
2.36	10.0	9.3		3.93 (4.0)
3.53	10.0	13.7		3.94 (4.0)
4.72	10.0	18.3		3.94 (4.0)
5.90	10.0	23.3		3.95 (3.8)
1.76	20.0		8.4	4.20
1.76	40.0		15.4	3.85
1.76	60.0		22.3	3.72
1.59	80.0		29.2	3.65
1.59	100.0		35.7	3.57
1.59	120.0		46.1	3.84
1.76	10.0		4.2	4.20
				Average 3.93 ± 0.16

* Values in parentheses were obtained from second-order plots.

Table 2. Pseudo-first-order rate constants at different $[\text{HClO}_4]$ in the $\text{Bi}^{\text{V}} + \text{H}_3\text{PO}_2$ reaction at 35°C , $[\text{Bi}^{\text{V}}] = 1.15 \times 10^{-3}$, $[\text{H}_3\text{PO}_2] = 2.0 \times 10^{-2}$, $[\text{Bi}^{\text{III}}] = 0.01$, $[\text{HF}] = 1.5$, and $I = 2.0 \text{ mol dm}^{-3}$

$[\text{HClO}_4]/\text{mol dm}^{-3}$	0.5	0.75	1.0	1.25	1.5
$10^4 k_1/\text{s}^{-1}$	8.4	13	16	20	24

Table 3. Effect on $10^4 k_1/\text{s}^{-1}$ of the variation of Bi^{III} at different $[\text{HClO}_4]$ and temperatures in the reaction of $\text{Bi}^{\text{V}} + \text{H}_3\text{PO}_2$ at $[\text{Bi}^{\text{V}}] = 1.12 \times 10^{-3}$, $[\text{H}_3\text{PO}_2] = 4.0 \times 10^{-2}$, $[\text{ClO}_4^-]_{\text{T}} = 2.0$, and $[\text{HF}] = 1.5 \text{ mol dm}^{-3}$

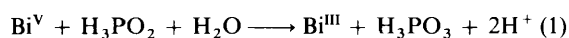
$\theta_c/^\circ\text{C}$	$[\text{HClO}_4]/\text{mol dm}^{-3}$	$10^3[\text{Bi}^{\text{III}}]/\text{mol dm}^{-3}$								
		0	0.4	1.4	2.4	3.4	4.4	6.4	8.4	10.4
25	1.0	3.8	4.2	5.0	5.75	—	7.3	8.3	—	8.4
35	1.0	20.5	21.5	23.5	25.5	27	29	32	34.5	—
45	1.0	28	32	42	50	—	69	77	79	81
35*	1.0	—	20	22	24	27	28	30	32	32
35	1.5	31	32	—	37	—	42	46	—	52
35	2.0	40	42	—	50	—	58	64	—	70

* Source of Bi^{III} was $\text{Bi}(\text{NO}_3)_3$.

Bismuth(v) solutions in a mixture of HClO_4 and HF containing both Bi^{V} and Bi^{III} absorb at 216 nm and the absorbance corresponds to a molar absorption coefficient of $1.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for Bi^{III} , a value similar to that obtained from Bi_2O_3 and to one reported earlier.³ This clearly shows that bismuth(v) complexes do not absorb in the u.v. region.

Results

Stoichiometry.—Reaction mixtures containing Bi^{V} and an excess of hypophosphite in the concentration range $(1-6) \times 10^{-3} \text{ mol dm}^{-3}$ were allowed to react for 4 h at 35°C . At the end of reaction the absence of Bi^{V} was confirmed iodometrically and the product, phosphite, was estimated iodometrically¹² in ammonium borate buffer after neutralizing HClO_4 and HF with NaOH. The amount of phosphite was always about 5–8% less than that of Bi^{V} taken initially according to equation (1). This difference may be ascribed to decomposition of Bi^{V} (over 4 h).



Bismuth(v) and H_3PO_2 Dependences.—The concentration of Bi^{V} was varied from 0.88×10^{-3} to $5.9 \times 10^{-3} \text{ mol dm}^{-3}$ and the order from the initial rates was found to be one. Hypophosphite was varied in the range $(10-120) \times 10^{-3} \text{ mol dm}^{-3}$ and a plot of the pseudo-first-order rate constant versus $[\text{H}_3\text{PO}_2]$ yielded a straight line passing through the origin. The order in H_3PO_2 is thus also one. A few second-order plots were also made. All the results are given in Table 1 and conform to the rate law (2) at fixed HClO_4 , HF, and Bi^{III} .

$$d[\text{Bi}^{\text{V}}]/dt = k_2[\text{Bi}^{\text{V}}][\text{H}_3\text{PO}_2] \quad (2)$$

Hydrogen-ion Dependence.—The hydrogen-ion concentration was varied with HClO_4 and the total perchlorate adjusted with LiClO_4 at fixed concentrations of the other reactants. A plot of the pseudo-first-order rate constant versus HClO_4 yielded a straight line passing through the origin. The results are given in Table 2.

Bismuth(III) and H_3PO_3 Dependences.—Since preliminary experiments indicated a catalytic effect of Bi^{III} on the rate of the $\text{Bi}^{\text{V}}-\text{H}_3\text{PO}_2$ reaction, the $[\text{Bi}^{\text{III}}]$ was systematically varied in the range $(1-10) \times 10^{-3} \text{ mol dm}^{-3}$, showing that the rate increases and tends to a limiting value. The results at three concentrations of HClO_4 and at three temperatures are given in Table 3. Since spectrophotometrically different species of Bi^{III} are indicated (depending on the source), $\text{Bi}(\text{NO}_3)_3$ was also employed as a source. However there was no difference in the kinetics results. That nitrate might exhibit a different form of species of Bi^{III} , but without effect on the rate, was proved by employing NaNO_3 in the concentration range $0.01-0.1 \text{ mol dm}^{-3}$ when the pseudo-first-order rate constants were unchanged. Zero concentration

of Bi^{III} in Table 3 means no added Bi^{III} , but the solutions always contained Bi^{III} along with Bi^{V} , less than about $5 \times 10^{-4} \text{ mol dm}^{-3}$.

Added H_3PO_3 in the range $(2-10) \times 10^{-3} \text{ mol dm}^{-3}$ had no effect on the rate.

A plot of k_1 or k_2 versus $[\text{Bi}^{\text{III}}]$, taking into account the Bi^{III} present in the sample of Bi^{V} , indicates that the empirical rate law (3) should hold at constant Bi^{V} , H_3PO_2 , and H^+ .

$$\frac{-d[\text{Bi}^{\text{V}}]}{dt} = A + \frac{B[\text{Bi}^{\text{III}}]}{C + D[\text{Bi}^{\text{III}}]} \quad (3)$$

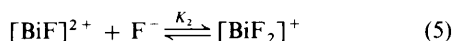
Effect of HF and Fluoride Ions.—The concentration of HF was varied in the range $0.5-1.5 \text{ mol dm}^{-3}$ but the rate was unaffected. Concentrations less than 0.5 mol dm^{-3} would have indicated the trend, if any, but it was not possible to employ such concentrations since Bi^{V} was not stable in low $[\text{HF}]$. The effect of fluoride ions was investigated by employing NaF in the range $0.01-0.1 \text{ mol dm}^{-3}$, but there was no change in the rate.

Discussion

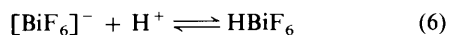
Hypophosphorous acid will remain completely undissociated in the highly acidic medium employed since its acid-dissociation constant is small.¹³

No information about the species of Bi^{V} and Bi^{III} is available from the kinetic data since there is no effect of HF and fluoride ions on the rate. Fluorohydroxo-complexes of Bi^{V} of the type $[\text{BiF}_x(\text{OH})_{6-x}]^-$ are said to exist³ purely on the basis that complexes of As^{V} and Sb^{V} are known^{14,15} to exist in such solutions. However, since the rate is not affected by the concentration of fluoride ions, either all the fluoro-species of Bi^{V} are equally reactive or a complex saturated with fluoride is formed in such solutions. We can assume that $[\text{BiF}_6]^-$ exists in the solutions employed in this investigation.

Bismuth(III) in HF solutions mainly exists¹⁶ as the cationic complexes $[\text{BiF}]^{2+}$ and $[\text{BiF}_2]^+$. Their concentrations are controlled by the acid-dissociation constants¹⁷ of HF and HF_2^- which are small, and the following equilibria (4) and (5) with $K_1 = 5 \times 10^4$ and $K_2 = 4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ at 25°C . Since there is no change in the u.v. spectrum of Bi^{III} upon variation of HF and no change in the rate either, Bi^{III} is likely to be in the form $[\text{BiF}_2]^+$. However, the forms of Bi^{III} and Bi^{V} do not matter so far as the kinetics are concerned.

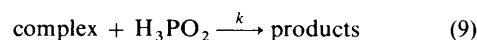
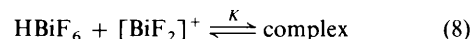
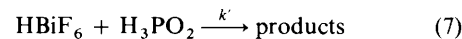


The dependences on $[\text{H}^+]$ and $[\text{Bi}^{\text{III}}]$ are relevant to the mechanism. In all probability, equilibrium (6) is operating. Thus the protonated species of Bi^{V} is reactive, rather than $[\text{BiF}_6]^-$.



Bismuth(III) has a catalytic role either in forming a mixed-valence complex of $\text{Bi}^{\text{V}}-\text{Bi}^{\text{III}}$ which is more reactive than Bi^{V} alone, or in forming a ternary complex with Bi^{V} and H_3PO_2 which undergoes redox reaction. It might be of interest that the hydrolysis¹⁸ of Sb^{V} in HCl is catalyzed by Sb^{III} and H^+ , which has been attributed to the Lewis-acid character of SbCl_3 or $[\text{SbCl}_4]^-$ and to the formation of a symmetrical transition state. A similar situation can be imagined in the present case too, with respect to catalysis by Bi^{III} in the form of the complex $[\text{BiF}_2]^+$.

Since a plot of k_1 versus $[\text{Bi}^{\text{III}}]$ has an intercept on the k_1 axis, the reaction between Bi^{V} and H_3PO_2 occurs also in the absence of Bi^{III} . Thus the mechanism in equations (6)–(9) may be suggested and the relationships (10)–(15) can be derived.



$$\frac{-d[\text{Bi}^{\text{V}}]}{dt} = K_p k' + \left(\frac{K_p K k [\text{Bi}^{\text{III}}]}{1 + K [\text{Bi}^{\text{III}}]} \right) [\text{Bi}^{\text{V}}][\text{H}_3\text{PO}_2][\text{H}^+] \quad (10)$$

$$= k_1 [\text{Bi}^{\text{V}}] \text{ at constant } \text{Bi}^{\text{III}}, \text{H}_3\text{PO}_2, \text{ and } \text{H}^+ \quad (11)$$

$$= k_2 [\text{Bi}^{\text{V}}][\text{H}_3\text{PO}_2] \text{ at constant } \text{Bi}^{\text{III}} \text{ and } \text{H}^+ \quad (12)$$

$$k_2 = K_p k' [\text{H}^+] + \frac{K_p K k [\text{Bi}^{\text{III}}][\text{H}^+]}{1 + K [\text{Bi}^{\text{III}}]} \quad (13)$$

$$k_0 = K_p k' + \frac{K_p K k [\text{Bi}^{\text{III}}]}{1 + K [\text{Bi}^{\text{III}}]} \quad (14)$$

$$k_0 - K_p k' = \frac{K_p K k [\text{Bi}^{\text{III}}]}{1 + K [\text{Bi}^{\text{III}}]} \quad (15)$$

Since the rate constant ($K_p k'$) at zero $[\text{Bi}^{\text{III}}]$ is known by extrapolation, a plot of $(k_0 - K_p k')^{-1}$ versus $[\text{Bi}^{\text{III}}]^{-1}$ can be made, yielding a straight line with a non-zero intercept. From this $K_p k$ ($\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) and K ($\text{dm}^3 \text{ mol}^{-1}$) were found to be 0.04 ± 0.003 and $58, 0.125 \pm 0.015$ and $45, 0.40 \pm 0.07$ and 66 at $25, 35, \text{ and } 45^\circ\text{C}$ respectively; K seems to be almost independent of temperature. The values of $K_p k$ ($\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) and K ($\text{dm}^3 \text{ mol}^{-1}$) from a similar plot at different hydrogen-ion concentrations were found to be 0.125 and $45, 0.166$ and $55, 0.22$ and 52 at $\text{H}^+ = 1.0, 1.5, \text{ and } 2.0 \text{ mol dm}^{-3}$ respectively.

The same rate law would be obtained if one assumed a weak complexing between Bi^{V} and H_3PO_2 and then further complexing with Bi^{III} . In any case direct complexation between Bi^{III} and H_3PO_2 is not indicated kinetically or spectrophotometrically.

From the analogy with antimony(V) complexes^{18,19} in HCl, Bi^{V} in HF solutions might be in the form $[\text{BiF}_6]^-$. Since hydrolysis²⁰ of $[\text{SbCl}_6]^-$ is slow, the hydrolysis of $[\text{BiF}_6]^-$ is likely to be still slower. Thus, in redox reactions of Bi^{V} , hydrolysis does not seem to be of significance.

Although by analogy²¹ with $[\text{Sb}(\text{OH})_6]^-$ one can assume a species $[\text{Bi}(\text{OH})_6]^-$, the solubility of the latter would be smaller, and its tendency to polymerize will be greater than that of $[\text{Sb}(\text{OH})_6]^-$. The solubility²² of $[\text{Sb}(\text{OH})_6]^-$ is itself small and it polymerizes²³ and hence the probability of obtaining Bi^{V} as $[\text{Bi}(\text{OH})_6]^-$ in solution is remote. Thus sodium bismuthate, the known compound of Bi^{V} , must be highly polymeric defying dissolution by any acid or alkali.

A previous study⁴ stated that HClO_4 solutions of Bi^{V} are surprisingly stable. Since we could not obtain HClO_4 solutions, it is difficult to comment on this. In any case such solutions are likely to be less stable than they are claimed to be. Moreover, the previous study assumed a rate-controlling equilibrium prior to the redox step involving the various reducing species. This equilibrium should exist even in the absence of a reductant and thus water should be oxidized if no reductant is present. Hence the mechanism proposed in the paper itself predicts the instability of HClO_4 solutions of Bi^{V} .

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