Kinetics of Oxidation-Reduction Reactions Between Elements of Groups V and VII. Part I. Bismuth(v) with Halide Ions and Other Reductants

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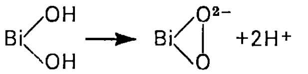
The oxidations of the ions I^-, Br^-, Cl^-, SCN^-, Tl^+, and $IrCl_6^{3-}$ by bismuth(v) in perchloric acid solution all obey the rate expression $-d[Bi^V]/dt = k[Bi^V]$, where $k = 161{\cdot}4 \pm 8{\cdot}0\ s^{-1}$ at $[H^+] = 0{\cdot}5$M, $I = 2{\cdot}0$M, and $t = 25$ °C. Rates of reaction are practically independent of $[H^+]$ in the range 0·5—2·0M. Measurements at four different temperatures give $E_a = 7{\cdot}1 \pm 0{\cdot}3$ kJ mol^{-1} and $\Delta S^\ddagger = -187 \pm 1$ J K^{-1} mol^{-1}. Mechanisms consistent with this data are discussed and that involving (i) as the rate-determining step is preferred. Potentiometric titrations


(i)

give $E^0 = 2{\cdot}03 \pm 0{\cdot}17$ V for the half-cell reaction $Bi^V + 2e \longrightarrow Bi^{III}$ at $[H^+] = 0{\cdot}5$M, $I = 2{\cdot}0$M, and $t = 25$ °C.

ALL elements of Group V exhibit the oxidation states III and V, the relative stabilities of which differ widely from element to element, as measured by electrode potential data.[1,2] The general oxidation-reduction reaction (1) (where X_2 and X^- represent a halogen molecule

$$M^{III} + X_2 \rightleftharpoons M^V + 2X^- \qquad (1)$$

and its ion) can have a large or a small equilibrium constant, depending on the identities of M and X. We have studied the kinetics of these reactions (most of which are quite rapid) for arsenic, antimony, and bismuth, using as reactants either M^{III} and X_2 or M^V and $2X^-$ depending on the equilibrium constant for reaction (1).

The aqueous chemistry of bismuth(III) has been little studied and almost no information has been published concerning bismuth(v) in aqueous solution. Latimer[2] calculated that the potential of the supposed couple $Bi_2O_4 + 4H^+ + 2e \longrightarrow 2BiO^+ + 2H_2O$ should be $E^0 = +1{\cdot}58$ V in acid solution, from early results obtained for the so-called Bi_2O_4–Bi_2O_3 couple in alkaline solution. Since there is no evidence that Bi^{IV} is a stable oxidation state of bismuth and therefore Bi_2O_4 must contain Bi^V and Bi^{III}, Latimer made the reasonable assumption that the Bi_2O_5–Bi_2O_3 potential would be similar to that reported for Bi_2O_4–Bi_2O_3.

Preliminary results of our study of the kinetics of the reaction of Bi^V with the ions I^-, Br^-, and Cl^- were published in a previous communication.[3] We now report our results in full for these and other reducing agents, including rate studies at different acid concentrations and temperatures.

EXPERIMENTAL

Bismuth(v) *Solutions in Perchloric Acid.*—These were prepared by adding solid sodium bismuthate (AnalaR), $NaBiO_3$, to 0·5M-perchloric acid, shaking the suspension in a conical flask protected from the light for about 10—20 min, and filtering. Solutions were stored for no longer than 2 days.

Bismuth(v) concentrations were determined by adding aliquot portions of Bi^V solution to an excess of potassium iodide solution and measuring the absorption due to formation of the resultant orange Bi^{III}–I^- complexes[4,5] at 450, 460, or 370 nm. Linear calibration curves of absorption against concentration were obtained using known concentrations of sodium bismuthate (in 2M-H_2SO_4 or -$HClO_4$) and Bi_2O_3 for two different iodide ion concentrations ($[I^-] =$ 0·042 and 0·173M). Nearly identical curves were obtained for Bi^{III} and Bi^V at 460 nm where absorption due to the ion I_3^- (generated by Bi^V) would not be expected to be significant. At 370 nm part of the observed absorption was attributed to I_3^-. Typical concentrations were $[Bi^V] = 10^{-4}$ and $[HClO_4] = 0{\cdot}5$M.

It was of crucial importance to ascertain whether these solutions prepared as Bi^V in fact contained Bi^V or had become reduced to Bi^{III}. The presence of the latter was tested for using dithiazone,[5] which is green in CCl_4 ($\lambda_{max.}$ 440 and 620 nm[6]). Bismuth(III) reacts with dithiazone to give the corresponding orange dithiazonate complex ($\lambda_{max.}$

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[1] 'Stability Constants of Metal-ion complexes,' 2nd edn., The Chemical Society, London, 1964; Sup. No. 1, 1971.

[2] W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice-Hall, New York, 1952.

[3] M. H. Ford-Smith and J. J. Habeeb, *Chem. Comm.*, 1969, 1445.

[4] G. Carlot and D. Bezier, 'Quantitative Inorganic Analysis,' Methuen, London, 1957.

[5] C. Merritt, H. M. Hershenson, and L. B. Rogers *Analyt. Chem.*, 1953, **25**, 572.

[6] G. Iwantscheff, *Angew. Chem.*, 1957, **69**, 472.

490 nm). Dithiazone solution (10 cm^3; 2·5 g AnalaR dithiazone in 250 cm^3 AnalaR CCl_4) was shaken with $3{\cdot}2 \times 10^{-4}$M-Bi^V (10 cm^3) in 0·5M-$HClO_4$. The spectrum of the dithiazone in CCl_4 was unchanged. Addition of a drop of $2{\cdot}6 \times 10^{-3}$M-Bi^{III} (AnalaR Bi_2O_3) in 0·5M-$HClO_4$ resulted in the appearance of an orange colour. We were able to detect the presence of 10^{-5}M-Bi^{III} in this way, and showed that at least 97% of the Bi^V was not reduced to Bi^{III} in solution.

Other Reagents.—AnalaR NaCl, NaBr, and NaI, reagent grade NaSCN, Laboratory reagent $TlNO_3$, and potassium hexachloroiridate(III) (Johnson, Matthey and Co. Ltd.) were used without further purification.

Sodium perchlorate solutions were prepared from AnalaR perchloric acid and sodium bicarbonate. Exact neutralisation was confirmed by performing acid–base titrations on dilute aliquot portions. Sodium perchlorate concentrations were estimated by passing an aliquot portion down a cation-exchange resin in the acid form and titrating the acid liberated with standard sodium hydroxide solution.

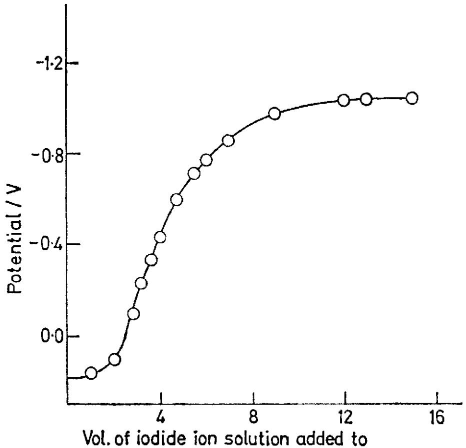
All kinetic studies were performed using a Durrum–Gibson stopped-flow spectrophotometer equipped with a Kel-F flow system and a deuterium lamp. Sodium perchlorate was used as the inert electrolyte to maintain the ionic strength at I = 2·0M.

RESULTS

Potentiometric Titrations.—An attempt was made to obtain a direct measurement of the Bi^V–Bi^{III} electrode potential in acid solution by performing potentiometric titrations of Bi^V solutions against iodide or bromide ion solutions. Calomel reference and platinum indicator electrodes were used, connected *via* a salt bridge of ammonium nitrate in agar gel.[7] During the course of the titrations a grey deposit appeared on the platinum electrode, which possibly consisted of $Pt(OH)_2$. [Oxidation of platinum by Bi^V is at least thermodynamically possible since for the $Pt(OH)_2$, $2H^+$–$Pt,2H_2O$ couple $E^0 = +0{\cdot}98$ V.] Experiments in which a gold indicator electrode was substituted for that of platinum resulted in more substantial attack on the electrode and no useful titration curves. A typical titration curve obtained with a platinum electrode is shown in the Figure. End-points in the titrations were obtained at titrant volumes which agreed quite closely with those calculated using the known concentration of the reagents and an assumed stoicheiometry for the reactions $Bi^V + 2X^- \longrightarrow Bi^{III} + X_2$ (X = Cl, Br, or I), indicating that the attack on the platinum electrode was not quantitatively significant.

Using the potentials at the end-points of the titrations, together with the literature values[1,8] $I_2(aq) + 2e \longrightarrow 2I^-(aq)$, $E^0 = 0{\cdot}627$ V and $Br_2(aq) + 2e \longrightarrow 2Br^-(aq)$, $E^0 = 1{\cdot}085$ V, we calculated the Bi^V–Bi^{III} electrode potential to be $+2{\cdot}03 \pm 0{\cdot}17$ V at 25 °C, $[H^+]$ = 0·5M, and I = 2·0M (2·05 V from five $Bi^V + I^-$ titrations and +1·98 V from three $Bi^V + Br^-$ titrations; $[Bi^V] = 1{\cdot}0 \times 10^{-4}$—$2{\cdot}05 \times 10^{-4}$, $[X^-] = 2{\cdot}0 \times 10^{-4}$—$8{\cdot}0 \times 10^{-4}$M). This value is much greater than Latimer's estimate[2] of +1·60 V. However the latter was based on an experimental measurement at $[OH^-]$ = 10M and an inadequate knowledge of the pH dependence of the electrode potential. The value $E^0 = +2{\cdot}0$ V means that Bi^V is one of the most powerful oxidising agents available in aqueous solution, comparable to the couples $S_2O_8^{2-}$–$2SO_4^{2-}$ (E^0 +2·01 V) and $O_3,2H^+$–O_2,H_2O (E^0 +2·07 V), and indicates that the oxidations of the ions I^-, Br^-, Cl^-, SCN^-, Tl^+, $IrCl_6^{3-}$, *etc.* by Bi^V should be quantitative.

Kinetics of the Reactions of Bi^V *with the Ions* I^-, Br^-, Cl^-, SCN^-, $IrCl_6^{3-}$, Tl^+, OCN^-, CN^-, N_3^-, *and* $Fe(bipy)_3^{2+}$.—The reactions with the singly charged anions I^-, Br^-, Cl^-, and SCN^-, $Bi^V + 2X^- \longrightarrow Bi^{III} + X_2$ (X = I, Br, Cl, or SCN), were followed by monitoring the increase in absorption corresponding to the formation of Bi^{III}–X^- complexes. The wavelengths of maximum absorption [460 (I^-), 365 (Br^-), 325 (Cl^-), and 275 nm (SCN^-), in good agreement with published values[5,9]] and pseudo-first-order conditions ($[X^-]_0$ at least ten times greater than $[Bi^V]_0$) were used. Plots of log ($A_\infty - A_t$) against time t (where A_t and A_∞ are the absorbances at times t and infinity) were excellently linear to at least 80% completion, indicating that the reactions were first order with respect to $[Bi^V]$. The pseudo-first-order rate constants, k_{1-4}, obtained from the slopes of such plots at a variety of initial X^- concentrations are listed in Table 1.



Potentiometric titration curve for the $Bi^V + 2I^- \longrightarrow Bi^{III} + I_2$ reaction. $[Bi^V]_0 = 2{\cdot}5 \times 10^{-4}$, $[I^-]_0 = 4{\cdot}5 \times 10^{-4}$, $[H^+]$ = 0·5, and I = 2·0M; t = 25 °C

No detectable spectral changes occurred when Bi^V was mixed with the pseudo-halide ions CN^-, OCN^-, and N_3^-. Presumably oxidation-reduction reactions do occur in these systems, but no reactant or product species absorbs strongly in the u.v. or visible region. We found in separate experiments that no absorbing species were produced when Bi^{III} was added to such solutions. Thus either Bi^{III} does not form complexes with these anions (which would be surprising) or the complexes have no strong visible or u.v. absorption band, in contrast to the situation with those of the ions I^-, Br^-, Cl^-, and SCN^-. Both Bi^V and Bi^{III} in perchloric acid have no measurable absorption so their concentrations cannot be monitored spectrophotometrically.

The reaction $Bi^V + 2IrCl_6^{3-} \longrightarrow Bi^{III} + 2IrCl_6^{2-}$ was followed by measuring the decrease in absorption at 485 nm accompanying the consumption of $IrCl_6^{3-}$. Concentrations of $IrCl_6^{3-}$ were in some experiments similar to or even less

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[7] W. G. Palmer, 'Experimental Physical Chemistry,' Cambridge University Press, Cambridge, 1949.

[8] G. Jones and S. Baeckstrom, *J. Amer. Chem. Soc.*, 1934, **56**, 1524.

[9] W. D. Kingery and D. M. Hume, *J. Amer. Chem. Soc.*, 1949, **71**, 2393.

than those of Bi^V, but good first-order plots were still obtained, giving values of k_6 (Table 1). The ion $Fe(dipy)_3^{2+}$ was found to be too unstable in acid solution for convenient use and the reaction was not studied in detail. The only complimentary reaction of the series, $Bi^V + Tl^I \longrightarrow Bi^{III} + Tl^{III}$, was followed by measuring the increase in absorption at 272 nm accompanying the production of Tl^{III}.

TABLE 1

Pseudo-first-order rate constants for the reaction of Bi^V with various reducing agents. $[H^+] = 0{\cdot}5$M; $I = 2{\cdot}0$M; $t = 25$ °C

Iodide				Bromide		Chloride		Thiocyanate		Thallium(I)		Hexachloroiridate-(III)	
$10^3[I^-]$ M	k_1 [a] s^{-1}	$10^3[I^-]$ M	k_1 [a] s^{-1}	$10^2[Br]$ M	k_2 [b] s^{-1}	$[Cl^-]$ M	k_3 [c] s^{-1}	$[SCN^-]$ M	k_4 [d] s^{-1}	$10^3[Tl^+]$ M	k_5 [e] s^{-1}	$10^4[IrCl_6^{3-}]$ M	k_6 [f] s^{-1}
2·0	149	16·0	161	1·5	161	0·011	163	0·01	158	2	157	0·68	163
3·0	148	20·0	168	4·0	158	0·06	158	0·025	160	13	161	3·4	169
4·0	168	24·0	164	8·0	159	0·07	161	0·04	161	40	157	17·0	161
6·0	173	24·0	158	10·0	163	0·10	166	0·125	159	80	163	43·0	162
8·0	186			25·0	160	0·24	160	0·25	164	100	164	170·0	151
10·0	148			45·0	159	0·50	166						
12·0	159					1·00	154						
			Av. = 162 ± 11		Av. = 160 ± 2		Av. = 161 ± 4		Av. = 161 ± 2		Av. = 160 ± 3		Av. = 161 ± 7

$[Bi^V]$/M = [a] $1{\cdot}6 \times 10^{-4}$. $7{\cdot}0 \times 10^{-5}$. [c] $1{\cdot}0 \times 10^{-4}$. [d] $9{\cdot}0 \times 10^{-5}$. [e] $1{\cdot}8 \times 10^{-4}$. [f] $1{\cdot}6 \times 10^{-4}$.

It is apparent from the data in Table 1 that (a) all the reactions have rates which are independent of reductant concentration, and (b) the reactions all occur at the same rate. For each reductant, log k was plotted against log [reductant], the gradients of the straight lines (equal to the order of the reaction with respect to reductant concentration) obtained being 0·032 ± 0·03 (I^-), −0·001 ± 0·003 (Br^-), −0·007 ± 0·012 (Cl^-), 0·007 ± 0·004 (SCN^-), −0·008 ± 0·005 (Tl^+), and −0·014 ± 0·007 ($IrCl_6^{3-}$). For all six reactions the first-order rate expression $-d[Bi^V]/dt = k[Bi^V]$ applied and the six first-order rate constants obtained were identical within the limits of experimental error ($k_1 = 162$, $k_2 = 160$, $k_3 = 161$, $k_4 = 161$, $k_5 = 160$, and $k_6 = 161$; average 161·4 ± 8·0 s^{-1}) and over a remarkably wide range of reductant concentration ($6{\cdot}8 \times 10^{-5}$—1·0M).

We selected the $Bi^V + Br^-$ reaction as the exemplary reaction to be used in further work because this system gave the most accurate data. The rate of the reaction was studied at various acid concentrations, rate constants obtained being listed in Table 2. It will be seen that the rate constant is essentially independent of $[H^+]$. A plot of log k against log $[H^+]$ had a slope of 0·012 ± 0·004. The very slight decrease in rate with decrease in $[H^+]$ is probably just significant and outside the limits of experimental error. A computer program was used to find the best fit of the experimental data to a rate expression of the form (2).

TABLE 2

First-order-rate constants for the $Bi^V + Br^-$ reaction at various $[H^+]$. $I = 2{\cdot}0$M, $t = 25$ °C, $[Br^-] = 1{\cdot}5 \times 10^{-2}$—$5{\cdot}0 \times 10^{-1}$M and $[Bi^V]_0 = 7{\cdot}0 \times 10^{-5}$—$1{\cdot}73 \times 10^{-4}$M

Number of runs	$[H^+]$/M	k/s^{-1}
6	0·5	160·2 ± 1·6
2	1·0	161·1 ± 1·6
2	1·5	162·4 ± 1·7
2	2·0	162·9 ± 0·9

$$\text{Rate} = [Bi^V](k' + k''[H^+] + k'''[H^+]^2, \textit{etc.}) \qquad (2)$$

The two-term expression Rate = $k'[Bi^V] + k''[Bi^V][H^+]$, with $k' = 159{\cdot}2$ s^{-1} and $k'' = 1{\cdot}9$ l mol^{-1} s^{-1}, was found to give the best fit. This means that, at $[H^+] = 1{\cdot}0$M, 98·8% of the reaction proceeds *via* the acid-independent path and only 1·2% *via* the acid-dependent path.

The rate constant for this reaction was also measured at four different temperatures (Table 3). A plot of log k against $1/T$ was linear and from the gradient and intercept we calculate, using the absolute rate equation $k = (e\boldsymbol{k}T/\boldsymbol{h})e^{\Delta S^\ddagger/R}\, e^{-E_a/RT}$, $E_a = 7{\cdot}1 \pm 0{\cdot}3$ kJ mol^{-1}, $\Delta H^\ddagger = 4{\cdot}6 \pm 0{\cdot}3$ kJ mol^{-1}, and $\Delta S^\ddagger = -187 \pm 1$ J K^{-1} mol^{-1}.

TABLE 3

First-order rate constants for the $Bi^V + Br^-$ reaction at different temperatures. $[Bi^V]_0 = 8{\cdot}0 \times 10^{-5}$, $[Br^-] = 0{\cdot}5$, $[H^+] = 0{\cdot}5$, and $I = 2{\cdot}0$M

t/°C	k/s^{-1}
5	102·2
5	115·2
15	138·8
15	138·8
25	160·2 ± 1·6
35	191·9
35	188·8

DISCUSSION

Bismuth(V) solutions in perchloric acid appear to be surprisingly stable. We have kept solutions protected from the light for *ca.* 5 days without observing significant decomposition. There seems to be no doubt that they contain Bi^V rather than $Bi^{III} + H_2O_2$ or $Bi^{III} + O_2$ (the expected decomposition products if Bi^V oxidised H_2O) since (a) we did not detect Bi^{III} by the dithiazone test, and (b) the kinetic results are incompatible with oxidation of our range of reductants by H_2O_2 or O_2 because H_2O_2 or O_2 would *not* give identical rate constants, nor would they give rates of reaction which were independent of reductant concentration.

The mechanism we proposed previously (X = Cl, Br,

$$Bi^V + H_2O \xrightleftharpoons{k_1} Bi^{IV} + OH\bullet + H^+ \qquad (3)$$

$$Bi^{IV} + X^- \xrightarrow{\text{fast}} Bi^{III} + X\bullet \qquad (4)$$

$$OH\bullet + X^- \xrightarrow{\text{fast}} OH^- + X\bullet \qquad (5)$$

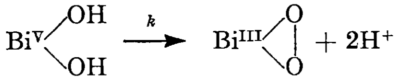
$$2X\bullet \xrightarrow{\text{fast}} X_2 \qquad (6)$$

I, and SCN),[3] while adequately accounting for the kinetic results, does not appear to be compatible with the observed stability of Bi^{V} solutions since it probably provides a path for rapid oxidation of H_2O by Bi^{V} in the absence of added reductant [equations (3), (7), and (8)],

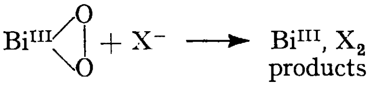
$$2OH\cdot \xrightarrow{\text{fast}} H_2O_2 \qquad (7)$$

$$2Bi^{IV} \xrightarrow{\text{fast}} Bi^{III} + Bi^{V} \qquad (8)$$

leading to the overall reaction $Bi^{V} + 2H_2O \longrightarrow Bi^{III} + H_2O_2 + 2H^+$. Because of this we prefer a mechanism which involves the production of a peroxo-complex of Bi^{III} instead of free hydroxyl radicals [equations (9) and (10)].

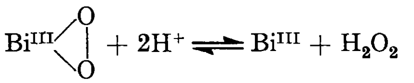


$$Bi^{V}(OH)_2 \xrightarrow{k} Bi^{III}(O_2) + 2H^+ \qquad (9)$$



$$Bi^{III}(O_2) + X^- \longrightarrow Bi^{III}, X_2 \text{ products} \qquad (10)$$

If Bi^{V} in perchloric acid is in the form $Bi(OH)_6^-$ (by analogy with H_5IO_6) then the peroxo-complex generated by reaction (9) would have the formula $Bi(OH)_4(O_2)^{3-}$. The essential difference between the two mechanisms is that the former [equations (3)—(6)] involves oxidation of free water molecules by Bi^{V}, while the latter [equations (9) and (10)] involves oxidation of co-ordinated water molecules (or hydroxide ions). If the second mechanism is not to lead to rapid decomposition of Bi^{V} solutions then it must be supposed that reaction (11) is either very slow or that it has a very small equilibrium



$$Bi^{III}(O_2) + 2H^+ \rightleftharpoons Bi^{III} + H_2O_2 \qquad (11)$$

constant. However, if our E^0 value for the Bi^{V}–Bi^{III} couple is seriously in error and the true value really should be close to Latimer's value of 1·6 V, then some of the force of the argument against the first mechanism would be lost since $H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$ has $E^0 = +1{\cdot}77$ V and the reaction $Bi^{V} + 2H_2O \rightleftharpoons Bi^{III} + H_2O_2 + 2H^+$ would then have a small instead of a large equilibrium constant.

The Arrhenius parameters for the reaction are unusual, with a nearly zero activation energy and a very large, unfavourable, entropy of activation. These parameters are difficult to reconcile with the first mechanism, which would be expected to have a large activation energy and a not very unfavourable entropy of activation. It may be significant that the Arrhenius parameters are very similar to ΔH^0 and ΔS^0 values often connected with acid dissociation,[1] *e.g.* for $H_3PO_4 \rightleftharpoons 2H^+ + HPO_4^{2-}$, $\Delta H^0 = -4{\cdot}6$ kJ mol^{-1} and $\Delta S^0 = -193$ J K^{-1} mol^{-1} and for $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$, $\Delta H^0 = +22{\cdot}2$ kJ mol^{-1} and $\Delta S^0 = -243$ J K^{-1} mol^{-1}. The similarity between the activation energy for our reaction and ΔH^0 values for these acids is probably fortuitous, but that between the entropy of activation and the (equilibrium) entropies for acid dissociation suggests that the type of rate-determining step we invoke may be correct, with the transition state resembling, in terms of hydration, the products of reaction (9).

We are able to reject mechanisms in which the rate-determining steps are the formation of Bi^{III}–X^- complexes (the absorptions were used to follow the reactions of Bi^{V} with the ions I^-, Br^-, Cl^-, and SCN^-). First, the reactions with the ions Tl^+ and $IrCl_3^-$ occur at the same rate as those with I^-, Br^-, Cl^-, and SCN^-, but they were ***not*** followed by monitoring the appearance of Bi^{III} or its complexes; with the ion $IrCl_6^{3-}$ it was possible to follow its rate of disappearance and with Tl^+ the formation of the product of oxidation (Tl^{III}) was followed. Secondly, it is inconceivable that rate constants for formation of the Bi^{III}–X^- complexes from Bi^{III} and X^- would be ***identical*** as would be required by our results, although it is possible that they are similar, as is found for anation reactions of cations with anions of the same charge.

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