

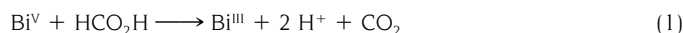
# Kinetics and Mechanism of Oxidation of Formic Acid by Bismuth(V) in Aqueous Phosphoric Acid Medium

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**ABSTRACT:** The solution of bismuth(V) was prepared by digesting sodium bismuthate in aqueous phosphoric acid (3.0 mol dm<sup>-3</sup>), the resulting pink colour solution absorbs in the visible region at 530 nm (640 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). The stoichiometry of the oxidation of formic acid by bismuth(V) corresponds to the reaction as represented by the Eq. (1).



The observed kinetic rate law is given by the Eq. (2)

$$-\frac{d[\text{Bi}^{\text{V}}]}{dt} = \left( k_1 + \frac{k_2 K_a}{[\text{H}^+]} \right) [\text{Bi}^{\text{V}}] [\text{HCO}_2\text{H}] \quad (2)$$

where Bi<sup>V</sup> and [HCO<sub>2</sub>H] are the gross analytical concentrations of bismuth(V) and formic acid respectively.

A plausible reaction mechanism corresponding to the rate law (2) has been proposed. Also the pattern of reactivity of bismuth(V) in HClO<sub>4</sub>-HF mixture and H<sub>3</sub>PO<sub>4</sub> respectively has been compared. © 2000 John Wiley & Sons, Inc. *Int J Chem Kinet* 32: 491–497, 2000

## INTRODUCTION

The solution chemistry of bismuth(V) is still not well understood despite the fact that the sodium bismuthate salt—a source [1–5] of bismuth(V)—has frequently been employed both in synthetic [6,7] and analytical [8] chemistry. The selective oxidation of corticosteroids by the reagent is considered a significant application in chromatographic analysis [9]. However, efforts have been made to bring bismuth(V) in solution phase; the problem of conveniently bringing bis-

muth(V) into the solution still remains unresolved. Burstein and Wright [10] first reported the solution of bismuth(V) in a mixture of HClO<sub>4</sub> (1.0 mol dm<sup>-3</sup>) and HF (1.52 mol dm<sup>-3</sup>), but the solutions are not very stable. The preparation of bismuth(V) solution (~10<sup>-4</sup> mol dm<sup>-3</sup>) in aqueous HClO<sub>4</sub> medium was also reported [11] without mentioning proper analytical conditions. However, our efforts to prepare the solution in aqueous perchloric acid were not successful.

## Bismuth(V) Solution

There is only one known [10] method that utilizes a mixture of HClO<sub>4</sub> and HF for digesting sodium salt of

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bismuthate to obtain bismuth(V) in the solution. Such solutions in  $\text{HClO}_4$ -HF mixture are not stable at ambient temperature and also contain bismuth(III) as an impurity. Moreover, the speciation of fluoro-bismuth(V) species in such solutions is yet to be resolved. Further, the method of standardization of this solution requires critical conditions. However, such problems to a large extent are not encountered for bismuth(V) solution in phosphoric acid medium.

The kinetic studies of the oxidation by bismuth(V) reported so far are, therefore, scanty [11–16]. The formation of bismuth(IV) and OH were considered to be the rate-determining step in one such study in perchloric acid medium where the rate was independent of the substrate concentration [11]. Recently, kinetics of oxidation of various compounds by bismuth(V) in  $\text{HClO}_4$ -HF mixtures have been reported [17], but the problem of speciation of bismuth(V) species still requires better resolution.

Our efforts in the past to bring bismuth(V) into the solution phase had not been successful; a limited success had, however, been achieved in dissolving sodium bismuthate in aqueous phosphoric acid. Nevertheless, such a solution of bismuth(V) has distinct advantages over the solution of the oxidant in  $\text{HClO}_4$ -HF mixture mainly from the viewpoint of avoiding the need to use HF.

The concentration of HF employed in bismuth(V) solution in  $\text{HClO}_4$ -HF mixtures rendered glasswares unserviceable and unusable due to the reaction of the silicate of the glass with HF.

## EXPERIMENTAL

Sodium bismuthate (Riedel AnalaR) was the source of bismuth(V), and the sample was employed as supplied without any further treatment. However, the sample of sodium bismuthate contained bismuth(III) oxide as an impurity, which can not be removed by any method or technique. Bismuth nitrate or bismuth oxide (BDH AnalaR) was employed for bismuth(III). Phosphoric acid was of E. Merck grade. Corning glassware was employed both for storing the solutions and the kinetics of the reactions unless specified otherwise.

Doubly distilled water was employed throughout the study; the second distillation was from alkaline permanganate solution in an all-glass apparatus.

The requisite quantity of sodium bismuthate was digested in aqueous  $\text{H}_3\text{PO}_4$  ( $3.0 \text{ mol dm}^{-3}$ ) solution for 20–30 minutes on a mechanical shaker; a pink solution with some undissolved material was obtained. Undissolved material was centrifuged and the solution was standardized iodometrically [12–15]. The solution is fairly stable if kept in brown glass bottles or

glass bottles blackened from the outside at refrigerated temperature ( $\sim 5^\circ\text{C}$ ). No traces of  $\text{H}_2\text{O}_2$  could be detected in such solutions even on long standing. Nevertheless, these solutions, similar to solutions in  $\text{HClO}_4$ -HF mixture, contained bismuth(III), which is either present as an impurity in the sample of bismuthate and/or formed during the digestion period of the solid through the reduction of bismuth(V) via oxidation of water to oxygen. It is, however, reported [8,17] that neither pentaoxide nor bismuthates can be prepared in a pure state but shall always contain a considerable amount of trivalent bismuth. Since bismuth(III) did not affect the kinetics of the title reaction, no efforts were made to remove bismuth(III) and the solutions were used as prepared.

## Spectrophotometric Analysis of the Solution

Bismuth(V) solution in  $\text{HClO}_4$ -HF mixture is transparent in the visible as well as in the ultraviolet region. Solution of bismuth(V) in aqueous phosphoric acid absorbs strongly in the visible region at 530 nm ( $\epsilon 640 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). This was done by taking solution of bismuth(V) in a 1-cm quartz cell against the reference of phosphoric acid present in the solution employing a spectrophotometer at  $\lambda 530 \text{ nm}$ .

## Kinetic Procedure

The requisite quantities of various components of the reaction mixture, except formic acid, were taken in glass-stoppered Erlenmeyer flasks, which were then suspended in a water bath thermostated at the desired temperature  $\pm 0.1^\circ\text{C}$  unless stated otherwise. The reaction was initiated by adding the requisite solution of the temperature pre-equilibrated formic acid into the reaction mixture, and the time of initiation was recorded when half of the contents from the pipette were released. Aliquot samples ( $5 \text{ to } 10 \text{ cm}^3$ ) were withdrawn at different intervals of time and then quenched in an ice-cold KI (10%) solution; the liberated iodine was titrated against thiosulphate solution using starch as an indicator. Measurements in triplicate without any interference from the ingredients of the reaction mixture were in agreement to within  $\pm 5\%$ .

Initial rates were computed employing plane mirror method [18]. Pseudo-first-order plots were also made wherever reaction conditions permitted. Since the kinetics is not affected by the light, no further precautions were taken to exclude light from the reaction mixtures.

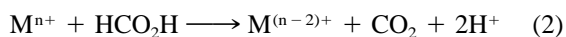
## Stoichiometry

The stoichiometry of the bismuth(V) and formic acid reaction in aqueous phosphoric acid medium was determined by undertaking certain reactions with an excess concentration of the oxidant over that of the substrate. The reactions were allowed to occur in a thermostated water bath at  $45 \pm 0.1^\circ\text{C}$  for 6 h; the excess of bismuth(V) was determined iodometrically (Table I).

The results in Table I show that the stoichiometry corresponds to the reaction as represented by the Eq. (1):



The evolution of  $\text{CO}_2$  gas was tested qualitatively by passing the gas in the freshly prepared lime water, which turned milky. However, it is generally accepted that formic acid is oxidized by metal ion oxidants to carbon dioxide, as represented by the Eq. (2):



## RESULTS

### Bismuth(V) Dependence

The concentration of bismuth(V) was varied from  $2.0 \times 10^{-4}$  to  $2.0 \times 10^{-3}$  mol dm $^{-3}$  at fixed formic acid concentrations, viz.  $2 \times 10^{-2}$ ,  $5 \times 10^{-2}$ , and  $1.0 \times 10^{-1}$  mol dm $^{-3}$ , respectively, and  $\text{H}_3\text{PO}_4 = 3.0$  mol dm $^{-3}$ . Pseudo-first-order plots were made and the first-order rate constants calculated from these plots were found to be independent of the initial concentrations of the oxidant (Table II).

### Formic Acid Dependence

Formic acid concentration was varied from  $2.0 \times 10^{-2}$  to  $1 \times 10^{-1}$  mol dm $^{-3}$  at different concentrations of Bi(V), viz.  $1.0 \times 10^{-3}$ ,  $1.25 \times 10^{-3}$ , and  $1.5 \times 10^{-3}$  mol dm $^{-3}$ , respectively, and  $\text{H}_3\text{PO}_4 = 3.0$  mol dm $^{-3}$ . Similarly formic acid concentration

**Table I** Stoichiometry of Bismuth(V) and Formic Acid Reaction in Aqueous Phosphoric Acid Medium

$10^3 \text{ Bi}^{\text{V}}$ Taken (mol dm $^{-3}$ )	$10^3 \text{ HCO}_2\text{H}$ Taken (mol dm $^{-3}$ )	$\Delta \text{HCO}_2\text{H}$ Used $\Delta \text{Bi}^{\text{V}}$ Used
1.0	0.5	0.98
1.5	1.0	0.98
2.0	1.0	0.97
2.0	1.5	0.97

**Table II** Pseudo First-Order and Second-Order Rate Constants in the Reaction of Formic Acid and Bismuth(V) in Aqueous Phosphoric Acid Medium.  $[\text{H}_3\text{PO}_4] = 3.0$  mol dm $^{-3}$ ,  $[\text{H}^+] = 1.0$  mol dm $^{-3}$ ,  $l = 2.0$  mol dm $^{-3}$ ,  $50^\circ\text{C}$

$10^3 \text{ Bi}^{\text{V}}$ mol dm $^{-3}$	$10^2 \text{ HCO}_2\text{H}$ mol dm $^{-3}$	$10^5 k'$ s $^{-1}$	$10^3 k$ dm $^3$ mol $^{-1}$ s $^{-1}$
0.2 (1.0)	2.0 (2.0)	4.4 (4.8)	2.2 (2.4)
0.4 (1.0)	2.0 (3.0)	4.4 (6.6)	2.2 (2.2)
0.5 (1.0)	2.0 (4.0)	4.6 (8.8)	2.3 (2.2)
0.7 (1.0)	2.0 (5.0)	4.6 (11.0)	2.3 (2.2)
0.8 (1.0)	2.0 (6.0)	4.8 (13.5)	2.4 (2.3)
1.0 (1.0)	2.0 (7.0)	4.8 (15.5)	2.4 (20.1)
1.25 (1.0)	2.0 (8.0)	4.8 (17.8)	2.4 (2.2)
1.50 (1.0)	2.0 (10.0)	4.4 (22.0)	2.2 (2.2)
1.75 (1.0)	2.0 —	4.4 —	2.2 —
0.2 (1.25)	5.0 (2.0)	11.0 (4.5)	2.2 (2.3)
0.4 (1.25)	5.0 (3.0)	11.5 (7.0)	2.2 (2.3)
0.6 (1.25)	5.0 (4.0)	11.2 (9.5)	2.2 (2.4)
0.7 (1.25)	5.0 (5.0)	10.7 (12.0)	2.2 (2.4)
0.8 (1.25)	5.0 (6.0)	12.0 (14.5)	2.4 (2.4)
1.0 (1.25)	5.0 (7.0)	12.0 (17.0)	2.4 (2.4)
1.25 (1.25)	5.0 (8.0)	12.0 (19.0)	2.4 (2.3)
1.50 (1.25)	5.0 —	12.0 —	2.4 (2.4)
2.0 —	5.0 (10.0)	12.0 —	2.4 —
1.5	2.0	4.8	2.4
1.5	3.0	7.4	2.4
1.5	4.0	9.1	2.3
1.5	5.0	12.2	2.4
1.5	6.0	13.3	2.2
1.5	7.0	14.5	2.2
1.5	8.0	17.6	2.2
1.5	10.0	20.2	2.1

$k$  in parenthesis is related to the concentrations of bismuth(V) and formic acid given in parenthesis in concentration columns.

was also varied in the above-stated range at  $45^\circ\text{C}$  at constant concentrations of other ingredients in the reaction mixture. The first-order rate constants increase proportionately with increasing concentration of formic acid commensurating first order with respect to formic acid (Table II).

Thus these results conform to the rate law, Eq. (3), at a fixed concentration of phosphoric acid:

$$-\frac{d[\text{Bi}^{\text{V}}]}{dt} = k[\text{Bi}^{\text{V}}][\text{HCO}_2\text{H}] \quad (3)$$

where  $k$  is an apparent second-order rate constant.

### Hydrogen Ion Dependence

Perchloric acid was employed to study the effect of hydrogen ion concentration on the rate of the reaction. Hydrogen ion concentration was varied from 0.5 to 2.0 mol dm $^{-3}$  at fixed concentrations of other re-

action ingredients, viz.  $\text{Bi}^{\text{V}} = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{HCO}_2\text{H} = 0.05 \text{ mol dm}^{-3}$ ,  $\text{H}_3\text{PO}_4 = 3.0 \text{ mol dm}^{-3}$ , and  $I = 2.0 \text{ mol dm}^{-3}$  (Ionic strength (I) was maintained constant by employing lithium perchlorate) at 40, 45, 50, and 55°C, respectively. The rate decreases with increasing concentration of hydrogen ion. However, hydrogen ion concentration contributed by phosphoric acid was also accounted for in subsequent calculations of the total hydrogen ion concentration in the reaction mixture.

Thus, if hydrogen ion dependence at constant concentrations of  $\text{Bi}^{\text{V}}$ ,  $\text{HCO}_2\text{H}$ , and  $\text{H}_3\text{PO}_4$ , respectively, is taken into account, the empirical rate Eq. (3) changes to Eq. (4):

$$-\frac{d[\text{Bi}^{\text{V}}]}{dt} = \left( A + \frac{B}{[\text{H}^+]} \right) [\text{Bi}^{\text{V}}] [\text{HCO}_2\text{H}] \quad (4)$$

where  $k = \left( A + \frac{B}{[\text{H}^+]} \right)$  and  $A$  and  $B$  are empirical rate constants.

Nevertheless, similar hydrogen ion dependence has also been observed in the kinetics studies of the oxidation of formic acid by reagents as diverse as permanganate and hexaquo-cobalt(III).

### Ionic Strength Dependence

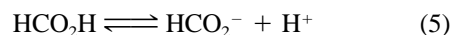
The effect of ionic strength on the rate was studied by varying the concentration of lithium perchlorate from 0.2 to 2.0  $\text{mol dm}^{-3}$  at  $\text{Bi}^{\text{V}} = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{HCO}_2\text{H} = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , and  $\text{H}_3\text{PO}_4 = 3.0 \text{ mol dm}^{-3}$ . The rate exhibits no change with changing concentration of lithium perchlorate.

### Bismuth(III) Dependence

The concentration of bismuth(III) over and above that already present in the solution of bismuth(V) was varied from 0.01 to 0.1  $\text{mol dm}^{-3}$  at  $\text{Bi}^{\text{V}} = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{HCO}_2\text{H} = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , and  $[\text{H}_3\text{PO}_4] = 3.0 \text{ mol dm}^{-3}$ . The rate remains unchanged with the changing concentration of bismuth(III). Such an effect of bismuth(III) is contrary to its effect observed in the oxidation of hypophosphorous acid by bismuth(V) in  $\text{HClO}_4$ -HF mixture [19]. Further, since bismuth(III) is one of the reaction products, the probability of any fast equilibrium involving bismuth(III) and preceded by the rate-determining step is ruled out.

## DISCUSSION

If the dissociation constant [20–22] of the formic acid is taken into account, the organic acid in aqueous phosphoric acid medium should be present both as molecular as well as dissociated forms governed by the equilibrium, Eq. (5):



Since the heats of ionization of formic acid [23] and other carboxylic acids are close to zero in the vicinity of 25°C, the value of ionization constant may be taken to be constant even at temperatures as high as 40°C. Further, the protonated formic acid such as  $\text{HCO}_2\text{H}_2^+$  in hydrogen ion concentrations employed in the kinetics studies is also ruled out, as the former has not been detected [34] even in the presence of higher concentrations of mineral acids [24–29]. It is, therefore, pertinent to assume  $\text{HCO}_2\text{H}$  and  $\text{HCO}_2^-$  to be the reactive forms of formic acid in view of the observed hydrogen ion dependence.

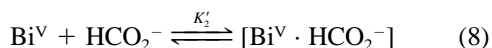
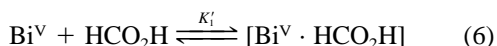
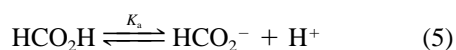
Further, the concentration of phosphoric acid in the reaction mixtures is significantly high. Information regarding the speciation of phosphato-bismuth(V) species in the solution can neither kinetically nor spectrally be ascertained. However, useful information related to phosphato-bismuth(V) species can be obtained on the pattern of fluoro-antimony(V) species in the solution only on the basis of their group affinity in the periodic table.

If one takes into account antimony(V) species [30–32], bismuth(V) by analogy might be in the form of phosphato or aquo-phosphato complexes. Since the hydrolysis [33] of  $[\text{SbCl}_6]^-$  is slow, the hydrolysis of phosphato-bismuth(V) is likely to be slower. Further, since the solubility of  $[\text{Sb}(\text{OH})_6]^-$  is small [34] and the species also polymerizes [35], the probability of bismuth(V) as  $[\text{Bi}(\text{OH})_6]^-$  in the phosphoric acid solution is highly remote. Also, the phosphate ions do not affect the rate; either all the phosphato-bismuth(V) species are equally reactive or bismuth(V) species are fully saturated by phosphate ions.

The Vth group elements in their valency shell have an electronic configuration of  $ns^2 np^3$ ; the lighter elements nitrogen and phosphorus exhibit covalent bonding in their compounds. However, the trend of increasing cationic character is exhibited by the heavier elements, such as antimony and bismuth. Although electron gain to achieve electronic structure of the next noble gas is conceivable, a considerable amount of energy is involved in such a process. It is probably the reason that cationic complexes, except that of nitro-

gen, are rare. Such an argument negates the probability of cationic phosphato-bismuth(V) species. Thus, the reactive form of bismuth(V) in phosphoric acid medium should be anionic, such as  $\text{Bi}(\text{PO}_4)_n^{(5-n)-}$ , in view of the large concentration of phosphoric acid. This species, heretofore, has been written as  $\text{Bi}(\text{V})$  for simplicity in analysis.

The hydrogen ion dependence is relevant to the mechanism of the reaction, and, in all probability, it comes from the formic acid. Further, the reaction is not catalyzed by bismuth(III); the latter, therefore, cannot become a part of the transition state. Considering all these observations and also accounting for the experimental findings, a probable reaction mechanism consisting of Steps (5)–(9) can be envisaged as follows:



Such a mechanism leads to the rate law (10):

$$\frac{-d[\text{Bi}^{\text{V}}]}{dt} = \left( k'_1 K'_1 + \frac{K_a k'_2 K'_2}{[\text{H}^+]} \right) \left( \frac{[\text{Bi}^{\text{V}}] [\text{HCO}_2\text{H}]}{1 + K'_1 [\text{HCO}_2\text{H}] + \frac{K_a K'_2}{[\text{H}^+]} [\text{HCO}_2\text{H}]} \right) \quad (10)$$

Since  $K_a$  is small,  $K'_1$  and  $K'_2$  are significantly small equilibrium constants. In view of the fact that the coordination sites of bismuth(V) are already blocked by phosphate ions and order with respect to formic acid is 1, the inequality

$$1 > \left( K'_1 [\text{HCO}_2\text{H}] + \frac{K_a k'_2}{[\text{H}^+]} [\text{HCO}_2\text{H}] \right)$$

is valid under experimental conditions.

This reduces the rate law (10) to (11) or (12):

$$\frac{-d[\text{Bi}^{\text{V}}]}{dt} = \left( k'_1 K'_1 + \frac{K_a k'_2 K'_2}{[\text{H}^+]} \right) [\text{Bi}^{\text{V}}] [\text{HCO}_2\text{H}] \quad (11)$$

$$\frac{-d[\text{Bi}^{\text{V}}]}{dt} = \left( k_1 + \frac{k_2 K_a}{[\text{H}^+]} \right) [\text{Bi}^{\text{V}}] [\text{HCO}_2\text{H}] \quad (12)$$

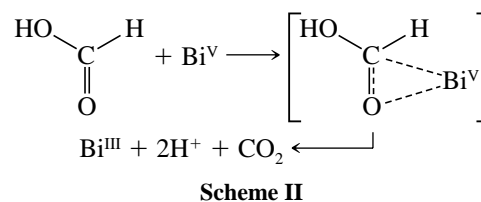
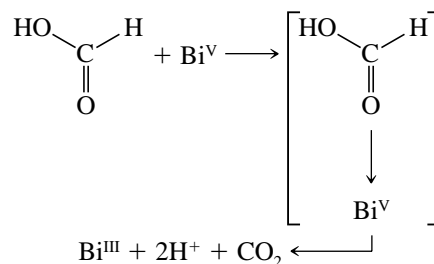
where  $\text{Bi}^{\text{V}}$  and  $\text{HCO}_2\text{H}$  are the gross analytical concentrations of bismuth(V) and formic acid, respectively, and  $k_1 = k'_1 K'_1$ ,  $k_2 = k'_2 K'_2$ . The rate law (12) is further reduced to Eq. (13):

$$k' = \left( k_1 + \frac{k_2 K_a}{[\text{H}^+]} \right) [\text{HCO}_2\text{H}] \quad (13)$$

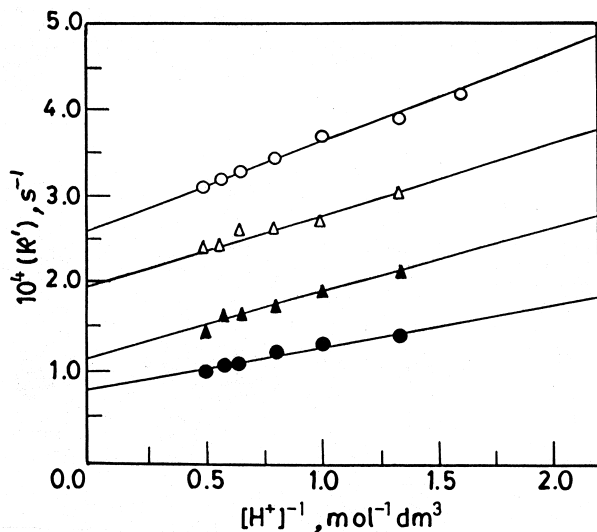
where  $k'$  is an observed pseudo-first-order rate constant.

A plot of  $k'$  vs.  $[\text{H}^+]^{-1}$  was made from the Eq. (13) that yielded a straight line with nonzero intercept (Fig. 1).  $k_1$  was calculated from the intercept to be  $1.6 \times 10^{-3}$ ,  $2.3 \times 10^{-3}$ ,  $3.9 \times 10^{-3}$ , and  $5.2 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and  $K_a k_2$  from the slope to be  $1 \times 10^{-3}$ ,  $1.5 \times 10^{-3}$ ,  $1.7 \times 10^{-3}$ , and  $2.1 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  at 40, 45, 50, and 55°C, respectively, and  $I = 2.0 \text{ mol dm}^{-3}$ . If  $K_a$  is taken into account, most of the reaction events are governed by the dissociated form of the organic acid.

So far as the mode of electron transfer from the substrate to the oxidant is concerned, the following reaction Scheme I or Scheme II can be proposed:



The oxidation of formic acid by  $\text{Np}(\text{VII})$  [8,36] in perchloric acid medium proceeds at a rate more rapid than the rate of the oxidation of organic acid by bismuth(V) in aqueous phosphoric acid medium. This suggests that the potential of  $\text{Bi}^{\text{V}}/\text{Bi}^{\text{III}}$  redox couple has less thermodynamic force than that of  $\text{Np}^{\text{VII}}/\text{Np}^{\text{VI}}$  re-



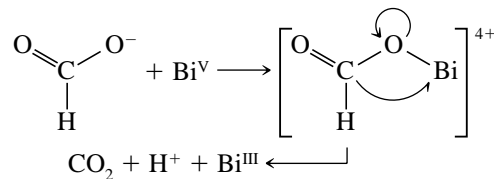
**Figure 1** Plot of  $K'$  vs.  $[H^+]^{-1} Bi^V = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $HCOOH = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $H_3PO_4 = 3.0 \text{ mol dm}^{-3}$ ;  $I = 2.0 \text{ mol dm}^{-3}$ . Temp. = ●, 40°C; ▲, 45°C; △, 50°C; ○, 55°C.

dox couple. Since the potential of  $Np^{VII}/Np^{VI}$  couple is  $>2.0 \text{ V}$ , the potential of  $Bi^V/Bi^{III}$  redox couple should certainly be  $<2.0 \text{ V}$ . Further, the rate of oxidation [24,37] of the organic acid by cerium(IV) in acid medium is less than that of the  $Bi(V)$ - $HCO_2H$  reaction. Likewise, the potential of  $Bi^V/Bi^{III}$  redox couple should be  $>1.5 \text{ V}$ , the potential of  $Ce^{IV}/Ce^{III}$  redox couple. On the basis of these observations, one can assume that the potential of  $Bi^V/Bi^{III}$  redox couple lies somewhere in the range  $1.5\text{--}2.0 \text{ V}$ . Since the potential of  $Bi^V/Bi^{III}$  redox couple in  $HClO_4$ -HF mixture is reported to be  $2.03 \pm 0.17 \text{ V}$ , the reaction of  $Bi^V$ - $HCO_2H$  in  $HClO_4$ -HF mixture takes place during the mixing period of the reagents. This also supports our contention that the potential of  $Bi^V/Bi^{III}$  redox couple is certainly less than  $2.03 \pm 0.17 \text{ V}$ . However, the reported [38] potential of  $Bi^V/Bi^{III}$  redox couple is  $1.58 \text{ V}$ . The range of potential as argued above quite agrees with this value.

If the redox potentials of one-equivalent and two-equivalent changes in formic acid or formate ion are taken into account, one electron transfer is favored only with very strong one-equivalent oxidants. It therefore appears reasonable in view of the absence of the free radicals in the reaction mixture that two-electron transfer in a single step of redox decomposition of the intermediate complex rather than one-electron transfer yielding bismuth(IV) and free-radical species of the organic acid is the preferred mode of the reaction. Since the redox potential of  $Bi^V/Bi^{III}$  couple in

$HClO_4$ -HF is appreciably higher than that of  $Bi^V/Bi^{III}$  couple in  $H_3PO_4$ , the possibility of bismuth(IV) diffusing out of the solvent cage is highly remote. Moreover, the addition of acrylic acid into the reaction mixture does not exhibit any polymerization, which further negates the presence of free radicals. Also, free radicals have not been indicated in other reactions of formic acid with two-equivalent oxidants.

Further, if the relative rates of  $HCO_2H$  and  $HCO_2^-$  species towards bismuth(V) are any guide, the latter species predominantly participates in the reaction. The mode of oxidation of formic acid by bismuth(V) in such an eventuality can also be assigned to the hydride ion transfer mechanism. This is supported by the fact that the energy advantage enjoyed by a two-electron transfer step is not available to the one-equivalent step in formation of an intermediate with high energy demand:



Also, the transfer of two electrons is more likely to induce structural changes; the hydride ion transfer involves the net transfer of charge between the reactants and products. An additional activation contribution due to the orientation of the solvent dipoles when reactants are converted to the products is also available to such a process.

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