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Kinetics and Mechanism of the Reduction of 12-Tungstocobaltate(III) by Formate. Catalysis by Alkali Metal Ions Through Outersphere Bridging

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Abstract

The kinetics of the reduction of 12-tungstocobaltate(III) by the molecular and anionic forms of formic acid follow the rate laws $-\mathrm{d}[\mathrm{Co^{III}M}]/\mathrm{d}t = 2k_1[\mathrm{Co^{III}M}]^2[\mathrm{HCOOH}]$ and $-\mathrm{d}[\mathrm{Co^{III}M}]/\mathrm{d}t = 2k_2[\mathrm{HCOO^-}][\mathrm{Co^{III}M}]_2$ respectively at a constant alkali metal ion concentration. Although the low pH rate (k_1) remains uninfluenced by the alkali cations, the magnitude of the apparent third-order rate constant (k_2) for the oxidation of formate ion largely depends on both the nature and the concentration of the cation present. The cation catalytic order, $K^+ > Na^+ > Li^+$, has been successfully explained with the help of the polarizability concept. A first-order dependence of k_2 on $[K^+]$ but second-order dependence on $[Na^+]$ and $[Li^+]$ is observed. These cation assisted paths have been studied thoroughly and the rate constants for these cation accelerated paths along with that for the spontaneous process have been evaluated. Activation parameters corresponding to the rate constants of the spontaneous and sodium ion assisted paths have been determined. A cation bridged outersphere electron transfer mechanism with the generation of free radicals is suggested.

Introduction

The photochemical generation of hydrogen by several 12-heteropolytungstates in the presence of a great variety of organic reagents has received considerable attention in recent years [1]. These polyanions are known to undergo multielectron reduction by chemical and electrochemical means [2–4]. The chemical reduction of 12-tungstocobaltate(III) (hereforth designated as $\mathrm{Co^{III}M}$ and the corresponding cobalt(II) species as $\mathrm{Co^{II}M}$) have also been the subject of recent studies by a wide range of thiols [5, 6], thiocyanate, iodide [7], hydroxylammonium ion [8] and ligands containing dihydroxyl groups [9] such as ascorbic acid, hydroquinone and catechol. We report here our findings on the reaction of $\mathrm{Co^{III}M}$ with formate where a significant cation catalysis phenomenon has been observed. Oxidative decarboxylation of formate is of significant interest because of its relevance to plant metabolism [10]. A number of plant leaves readily catalyse the oxidation of formate to carbon dioxide which can be fixed photosynthetically. Moreover, the uptake and translocation of cations by plants is a problem of continuing interest [11]. Thus the intimate mechanisms by which (i) leaves catalyse the conversion of formate into carbon dioxide, and (ii) the plants respond to excess levels of cations are still not quite clear. The electron transfer mechanism invoked in the present study may throw some light on these problems.

Experimental

Materials

Potassium salts of 12-tungstocobaltate(III), $[\mathrm{CoW_{12}O_{40}}]^{5-}$, and 12-tungstocobaltate(II), $\mathrm{CoW_{12}O_{40}}]^{6-}$, were prepared and characterized in the same way as reported by McAuley and coworkers [9] and were standardized following the procedure of Rasmussen and Brubaker [12]. Doubly recrystallized sodium formate was used to prepare stock solution. In some sets of experiments distilled formic acid was also used. Cation variation studies were performed using recrystallized sodium perchlorate, sodium nitrate, sodium sulphate, potassium nitrate and lithium perchlorate. The pH was adjusted with the respective acid (perchloric, nitric or sulphuric acid) and carbonate free alkali solution** (sodium, potassium or lithium hydroxide).

Measurements

A Pye-Unicam SP8-150 spectrophotometer, equipped with thermostated cell holders, was used to monitor the reaction by observing the decrease in absorbance at the absorption maximum of $\mathrm{Co^{III}M}$

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**No external buffer was added to adjust the pH. Excess formate present was sufficient to fix up the pH within ±0.02.

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(ϵ_{max}^{388} = 1155 ± 5 M^{-1} cm^{-1}). Some kinetic experiments were also conducted at 625 nm, the peak for $Co^{II}M$ having ϵ_{max} = 204 ± 3 M^{-1} cm^{-1}. Identical results were obtained at both wavelengths. Dissolved oxygen did not show any observable kinetic effect. pH measurements were done on a Systronics digital (model 335, India) pH meter.

Polymerization experiment

5% *v*/*v* acrylonitrile was added in each of the two deaerated vials containing $Co^{III}M$ and formate at 30 °C and at pH 1.5 and 5.0 respectively. Within a few minutes of mixing a cloudy suspension formed and after a lapse of one hour a large amount of precipitate was observed in both the vials. Blank experiments, from which either $Co^{III}M$ or formate was excluded, gave no detectable polymerization during this time demonstrating that the reaction of $Co^{III}M$ with both the protonated and dissociated forms of formic acid proceeds via the generation of free radicals.

Stoichiometry and Reaction Products

The stoichiometry of the reaction, determined sepctrophotometrically, can be represented as

$$2Co^{III}M + HCOOH \longrightarrow 2Co^{II}M + CO_2 + 2H^+ \qquad (1)$$

or

$$2Co^{III}M + HCOO^- \longrightarrow 2Co^{II}M + CO_2 + H^+ \qquad (2)$$

The stoichiometry is consistent with the observation that when $Co^{III}M$ was allowed to react with formic acid (or formate ion) in greater than 2:1 mole ratio, the ratio of $Co^{II}M$ formed/HCOOH (or $HCOO^-$) consumed was always 1.98 ± 0.03. The $Co^{II}M$ was characterized by its known absorbance at 625 nm. The only detectable gaseous product was carbon dioxide.

Results and Discussion

Kinetics

The absence of appreciable amounts of reaction intermediate can be inferred from the spectral changes observed during the reaction of $Co^{III}M$ with formate (pH 3.5–5.5) which showed a clear isosbestic point at 510 nm. Inspite of the large excess of [formate] (0.2–1.7 M) used with respect to $[Co^{III}M]$ (2 × 10^{-4} M), plots of $-\log(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbances at time *t* and infinity respectively, are all curved. Rather plots of $\Delta\epsilon/(A_t - A_\infty)$ *vs.* time, where $\Delta\epsilon$ is the difference in molar extinction coefficients for $Co^{III}M$ and $Co^{II}M$ species at the experimental wavelength (388 nm), were always linear up to >90% of the reaction, showing a second-order dependence on $[Co^{III}M]$ (Fig. 1). Values of the pseudo-second-order rate constant, k_{obs}, were obtained from the slope of the plots similar to that shown in Fig. 1. The intercepts of the plots similar to that in Fig. 1 are in good agreement with the corresponding reciprocal of the concentration of $Co^{III}M$ initially present.

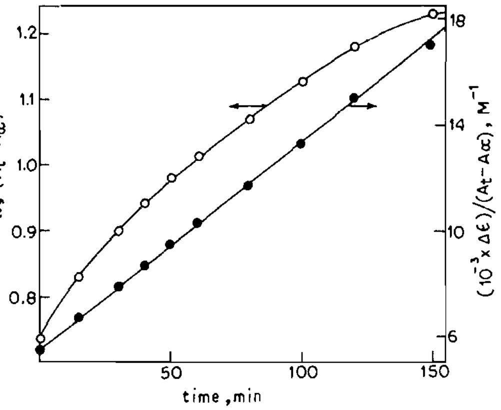

Fig. 1. Plots of $-\log(A_t - A_\infty)$ *vs.* time (open circles) and $\Delta\epsilon/(A_t - A_\infty)$ *vs.* time (filled circles) for a representative run at 70 °C. $[Formate]_T$ = 0.5 M, $[Na^+]_T$ = 1.7 M, $[Co^{III}M]$ = 2 × 10^{-4} M, pH = 5.20.

Dependence on [Formate]

The formate variation studies were performed at 60 °C, pH = 1.0 and 5.2, at constant $[Na^+]$ (1.0 M) and the results are shown in Table I. It should be

TABLE I. Observed Pseudo-Second-Order Rate Constants[a] as a Function of $[Formate]_T$

pH	$[Formate]_T$ (M)	$10^2 k_{obs}$ (M^{-1} s^{-1})	$10^2 k_{obs}/[Formate]_T$ (M^{-2} s^{-1})
1.00	0.20	1.14	5.70
	0.50	2.75	5.50
	0.80	4.55	5.69
	1.10	6.24	5.67
	1.40	7.75	5.54
	1.70	9.50	5.59
	$10^2 k_1$ = 2.81 ± 0.06 M^{-2} s^{-1}		
5.20	0.2	6.29	31.45
	0.4	12.75	31.88
	0.5	15.68	31.36
	0.6	18.54	30.90
	0.8	24.93	31.16
	1.0	30.44	30.44
	$10^2 k_2$ = 15.60 ± 0.38 M^{-2} s^{-1}		

[a] $[Na^+]_T$ = 1.0 M, $[Co^{III}M]$ = 2 × 10^{-4} M, 60.0 °C.

TABLE II. Apparent Third-Order Rate Constants in Different Media at 60 °C, $[\text{Formate}]_T = 0.5$ M and $[A^+] = 1.0$ M[a]

Medium	$10^2\ k_1$ ($M^{-2}\ s^{-1}$)	$10^2\ k_2$ ($M^{-2}\ s^{-1}$)
$LiClO_4$	5.59	1.19
$NaClO_4$	5.62	1.70
$NaNO_3$	5.67	1.73
Na_2SO_4	5.58	1.68
KNO_3	5.60	3.85

[a] A = Li, Na and K.

mentioned here that the concentration of alkali cation, not the ionic strength, was kept constant in these studies since the rates of these types of reactions are greatly influenced by the alkali metal ion concentration [13, 14]. It is evident from Table I that the pseudo-second-order rates exhibit first-order dependence on both [HCOOH]* and $[HCOO^-]$. Considering the stoichiometry, the rate laws for reactions (1) and (2) are given by eqns. (3) and (4).

$$d[Co^{II}M]/dt = 2k_1[Co^{III}M]^2[HCOOH] \qquad (3)$$

$$d[Co^{II}M]/dt = 2k_2[Co^{III}M]^2[HCOO^-] \qquad (4)$$

The values of k_1 and k_2 were obtained from the plots of k_{obs} *vs.* [HCOOH] and $[HCOO^-]$ respectively and are also collected in Table I.

Effect of Specific Ions on Reaction Rates

Anticipating specific cation catalysis analogous to that observed in oxalate oxidation [13], we studied the effects of specific ions on the rate of this electron transfer reaction by using salts of selective cations and anions as the supporting media. The results are presented in Table II. It is evident from Table II that the rates are quite independent of the nature of anions for both reactions (1) and (2). The cations also have no influence on the low pH rates, but they do have at high pH, *i.e.* for the oxidation of formate ion by $Co^{III}M$. The cation catalytic order is $K^+ > Na^+ > Li^+$.

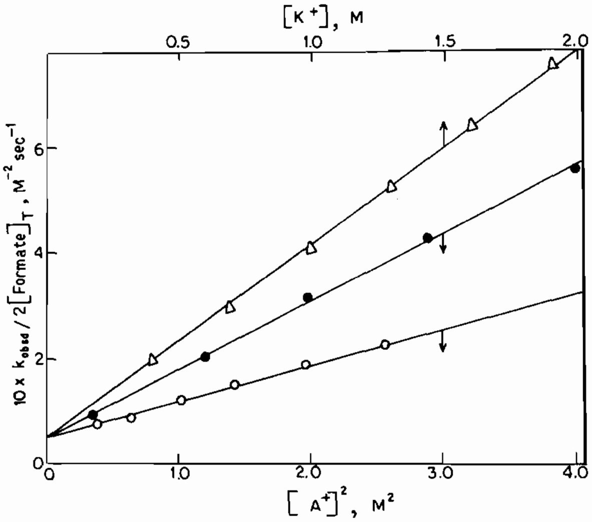

Fig. 2. Apparent third-order rate constant, $k_{obs}/2[\text{Formate}]_T$, as function of $[Li^+]^2$ (open circles), $[Na^+]^2$ (filled circles), and $[K^+]$ (open triangles) at 60 °C and pH = 5.20.

The individual effects of K^+, Na^+ and Li^+ ions on the reaction rate were studied thoroughly at pH 5.2. An important feature of this study is the different types of dependence of k_2 on these alkali metal ion concentrations. Although the plot of k_2 *vs.* $[K^+]$ was a perfect straight line, the plots of k_2 *vs.* $[Na^+]$ and $[Li^+]$ showed an upward curvature, and straight lines were obtained by plotting k_2 *vs.* $[Na^+]^2$ and $[Li^+]^2$ (Fig. 2). Thus the modified rate laws for reaction (2) in K^+, Na^+ and Li^+ can be expressed by eqns. (5), (6) and (7) respectively,

$$k_2 = k^\circ_2 + k'''_2[K^+] \qquad (5)$$

$$k_2 = k^\circ_2 + k''_2[Na^+]^2 \qquad (6)$$

$$k_2 = k^\circ_2 + k'_2[Li^+]^2 \qquad (7)$$

where $k_2 = k_{obs}/2[HCOO^-]$. The cation catalysed rates, obtained from the slopes of the plots in Fig. 2, are $k'_2 = (7.04 \pm 0.34) \times 10^{-2}\ M^{-4}\ s^{-1}$, $k''_2 = (12.89 \pm 0.30) \times 10^{-2}\ M^{-4}\ s^{-1}$ and $k'''_2 = (36.34 \pm 1.98) \times 10^{-2}\ M^{-3}\ s^{-1}$. The validity of these rate laws is further verified by the common intercept $\{=(4.68 \pm 0.33) \times 10^{-2}\ M^{-2}\ s^{-1}\}$ which actually represents the rate of the uncatalysed path (k°_2) for reaction (2). Figure 2 shows, in fact, that eqns. (5), (6) and (7) quantitatively describe all of these salt effect results remarkably well, considering that constant ionic strength was not maintained. The intrinsic effect of ionic strength alone on the reaction was however verified by using a mixture of $AClO_4$ (or ANO_3) and A_2SO_4 instead of only $AClO_4$ or ANO_3 (A = K, Na or Li). Fortunately, this effect need not be invoked to quantitatively understand the cation promoted redox interaction.

The simplest reaction scheme involves the initial formation of a free radical bound activated species, $[Co^{II}MHCO_2^{\bullet}]^{\neq}$, which then reacts with another molecule of $Co^{III}M$ to produce the reduced polyanion.

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*Since the p*k* of formic acid is 3.75 at 25 °C [15], it can be assumed that HCOOH does solely contribute to the redox process at lower pH (1.0). The molecular form of oxalic acid ($H_2C_2O_4$) however did not show any reactivity towards this substrate [13].

$$\mathrm{Co^{III}M^{5-} + HCOOH \xrightleftharpoons{K_A} Co^{III}M^{5-}, HCOOH} \qquad (8)$$

$$\mathrm{Co^{III}M^{5-}, HCOOH \xrightleftharpoons{K_B} [Co^{II}M^{6-}, HCOO^{\bullet}]^{\neq} + H^+} \qquad (9)$$

$$\mathrm{[Co^{II}M^{6-}, HCOO^{\bullet}]^{\neq} + Co^{III}M^{5-} \xrightarrow{k_a} 2Co^{II}M^{6-} + CO_2 + H^+} \qquad (10)$$

On this basis the theoretical rate expression is given by eqn. (11).

$$\mathrm{d[Co^{II}M]/d}t = 2k_aK_AK_B\mathrm{[Co^{III}M]^2[HCOOH]} \qquad (11)$$

This rate expression agrees with the rate law (eqn. (3)) observed for the cation independent formic acid oxidation. Comparing eqn. (3) with eqn. (11) we have $k_1 = k_aK_AK_B$. But in the oxidation of formate ion ($\mathrm{HCOO^-}$), in addition to the spontaneous reaction there also exists a cation assisted path. In the presence of $\mathrm{K^+}$ ion the mechanism of formate ion oxidation is represented by eqns. (12)–(18) with the corresponding rate expression as in eqn. (19).

$$\mathrm{Co^{III}M^{5-} + HCOO^- \xrightleftharpoons{K_C} Co^{III}M^{5-}, HCOO^-} \qquad (12)$$

$$\mathrm{Co^{III}M^{5-}, HCOO^- \xrightleftharpoons{K_D} [Co^{II}M^{6-}, HCOO^{\bullet}]^{\neq}} \qquad (13)$$

$$\mathrm{[Co^{II}M^{6-}, HCOO^{\bullet}]^{\neq} + Co^{III}M^{5-} \xrightarrow{k_b} 2Co^{II}M^{6-} + CO_2 + H^+} \qquad (14)$$

$$\mathrm{Co^{III}M^{5-} + K^+ \xrightleftharpoons{K_E} KCo^{III}M^{4-}} \qquad (15)$$

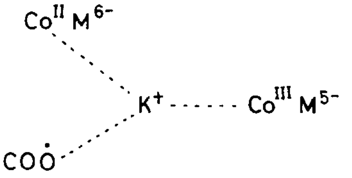
$$\mathrm{KCo^{III}M^{4-} + HCOO^- \xrightleftharpoons{K_F} KCo^{III}M^{4-}, HCOO^-} \qquad (16)$$

$$\mathrm{KCo^{III}M^{4-}, HCOO^- \xrightleftharpoons{K_G} [KCo^{II}M^{5-}, HCOO^{\bullet}]^{\neq}} \qquad (17)$$

$$\mathrm{[KCo^{II}M^{5-}, HCOO^{\bullet}]^{\neq} + Co^{III}M^{5-} \xrightarrow{k_c} K^+ + 2Co^{II}M^{6-} + CO_2 + H^+} \qquad (18)$$

$$k_{\mathrm{obs}} = 2(k_bK_CK_D + k_cK_EK_FK_G\mathrm{[K^+]})\mathrm{[HCOO^-]} \qquad (19)$$

From a comparison of eqns. (4), (5) and (19) one obtains $k^{\circ}_2 = k_bK_CK_D$ and $k'''_2 = k_cK_EK_FK_G$. The rate determining step (18) for the catalysed process may lead to transition state of the type



With $\mathrm{Na^+}$ and $\mathrm{Li^+}$ the reaction scheme is identical to that for $\mathrm{K^+}$, the only exception being the second-order dependence of k_2 on $\mathrm{[Na^+]}$ and $\mathrm{[Li^+]}$ which presumably requires a transition state of the type $\mathrm{Co^{III}M^{5-}\cdots A^+\cdots Co^{II}M^{6-}\cdots A^+\cdots HCOO^{\bullet}}$ (A = Na, Li).

Two important conclusions which emerge from the above discussions are that (i) the precursor equilibrium constants must be very small, *i.e.* the equilibrium is attained very rapidly compared to the rate determining step since no rate saturation was observed at high $\mathrm{[formate]_T}$ and (ii) the association or complexation has no effect on the optical density of $\mathrm{Co^{III}M}$ species, consistent with the observed isosbestic behaviour. It should be mentioned here that the outersphere equilibrium association has been suggested [5] to be operative in the oxidations of L-cysteine, mercaptoacetic acid and β-mercaptoethylamine by this cobalt(III) substrate. Oxidations of ascorbic acid, hydroquinone and catechol by $\mathrm{Co^{III}M}$ have also been found to occur [9] by a rapid preequilibrium of the reacting species.

The most striking feature of the present study is the second-order dependence of rate on the [oxidant] although a large excess ($>10^3$) of reductant is present. This fact, alongwith the other interesting observation, namely the formation of free radical in the course of the reaction, strongly supports the validity of the proposed mechanism. Considering the reaction scheme presented, it is likely that radical traps could change the reaction order in $\mathrm{[Co^{III}M]}$. Keeping this in mind we tried to perform some experiments using some free radical traps that do not give insoluble polymers (e.g., acrylamide). Unfortunately our attempt was unsuccessful since these free radical traps were found themselves to be reactive towards this cobalt(III) polyanion.

Thus our studies on the effect of alkali metal ions on the rate of electron transfer between anionic substitution inert $\mathrm{[Co^{III}W_{12}O_{40}]^{5-}}$ with $\mathrm{HCOO^-}$ exhibit a convincing evidence that cations can accelerate electron transfer. The large rate enhancement by the alkali cations can not be explained by a simple increase in the encounter rate due to shielding of the electrostatic repulsion between the negatively charged ions [16]. Similar cation catalytic order has been noticed by Rasmussen and Brubaker in the electron exchange reaction between $\mathrm{Co^{III}M}$ and $\mathrm{Co^{II}M}$ [12] and the faster exchange in $\mathrm{K^+}$ medium compared to that in $\mathrm{Li^+}$ has been ascribed to the increased ion-pairing by the larger $\mathrm{K^+}$ ion. In the model presented for the present system the main factors playing the dominant role in catalysing the reaction are polarizability and the difference in complexation constants. The greater polarizability of the large cations [17] is in accord with their increased catalytic activity and supports this model. Similar effects of cations on the rate of electron transfer have been encountered in the reduction of the same polyanion by oxalate [13], the oxidation of thiosulphate ions by octacyanotungstate(V) [18] and in many other redox processes [14, 19–23]. The second-order behaviour of the observed rate (k_2) on [Na$^+$] and [Li$^+$] but a linear dependence on [K$^+$] have also been observed by us [13] in the oxidation of oxalate with the same substrate and by Sulfab *et al.* [24] in the oxidation of hexacyanoferrate(II) with tris(malonato)cobaltate(III) at high cation concentrations.

Effect of Excess [Co^{II}M] on Reaction Rate

Some kinetic runs were carried out in the presence of Co^{II}M ions at concentrations of five times the initial concentration of Co^{III}M at pH 5.20. It was found that the addition of Co^{II}M to the reaction mixture has a slight (20%) inhibitory effect, but this is not large enough to cause interference with the kinetics in the absence of added Co^{II}M since amounts of Co^{II}M produced in the reaction are stoichiometric.

This fall of rate in the presence of excess Co^{II}M is not unexpected since the excess Co^{II}M^{6-}, with its high negative charge, can trap the alkali metal ions forming ion pairs, thus decreasing the effective alkali cation concentration in the reaction mixture.

pH Dependence

The pH variation studies were carried out at 60 °C keeping the concentrations of the reactants constant ([formate]$_T$ = 0.05 M and [Na$^+$]$_T$ = 1.0 M). Taking into account the contributions of both formic acid and formate ion towards the rate of the reaction and considering eqns. (3) and (6) the rate eqn. (20) can be derived where K_1 represents the dissociation constant of formic acid. As shown in Fig. 3 the pH-rate profile gives an excellent fit to

$$\frac{d[\mathrm{Co^{II}M}]}{dt} = 2[\mathrm{Co^{III}M}]^2[\mathrm{formate}]_T \times \left\{ \frac{k_1[\mathrm{H^+}] + K_1(k^\circ_2 + k''_2[\mathrm{Na^+}]^2)}{(K_1 + [\mathrm{H^+}])} \right\} \quad (20)$$

eqn. (20) with the experimental k_1, k°_2 and k''_2 values with a value of $K_1 = 3.16 \times 10^{-4}$ M which is in good agreement with that mentioned in the literature [15] under comparable conditions.

Activation Parameters

The temperature dependence studies were performed at a fixed pH (= 5.2) varying the cation (Na$^+$) concentration at a constant [formate]$_T$ and the results are summarized in Table III. Table III also includes the values of k$^\circ_2$ and

TABLE III. Pseudo-Second-Order Rate Constants as a Function of [Na$^+$] and Temperatures at pH = 5.20 and [Formate]$_T$ = 0.5 M

Temperature (°C)	[Na$^+$] (M)	$10^2\ k_{obs}$ (M^{-1} s^{-1})
50.0	0.5	2.10
	0.7	2.55
	0.9	4.08
	1.1	5.65
	1.3	7.90
$k^\circ_2 = (0.79 \pm 0.05) \times 10^{-2}$ M^{-2} s^{-1}, $k''_2 = (4.13 \pm 0.11) \times 10^{-2}$ M^{-4} s^{-1}		
60.0	0.6	8.49
	1.1	19.92
	1.4	31.58
	1.7	42.50
	2.0	55.19
$k^\circ_2 = (4.68 \pm 0.19) \times 10^{-2}$ M^{-2} s^{-1}, $k''_2 = (12.89 \pm 0.34) \times 10^{-2}$ M^{-4} s^{-1}		
70.0	0.5	25.80
	0.8	45.09
	1.1	69.62
	1.4	104.40
	1.7	129.00
$k^\circ_2 = (19.65 \pm 0.78) \times 10^{-2}$ M^{-2} s^{-1}, $k''_2 = (39.66 \pm 1.05) \times 10^{-2}$ M^{-4} s^{-1}; $\Delta H^\circ{}_2^{\ddagger} = 34.83 \pm 3.96$ kcal mol^{-1}, $\Delta S^\circ{}_2^{\ddagger} = 39.25 \pm 6.81$ e.u; $\Delta H''{}_2^{\ddagger} = 24.30 \pm 0.73$ kcal mol^{-1}, $\Delta S''{}_2^{\ddagger} = 9.84 \pm 0.80$ e.u.		

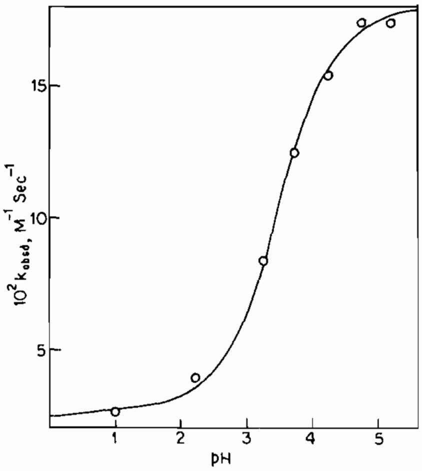


Fig. 3. pH–Rate profile. [Formate]$_T$ = 0.5 M, [Na$^+$]$_T$ = 1.0 M, at 60 °C. The curve was drawn through calculated values of k_{obs}, obtained from eqn. (20) using the values of k_1, k°_2 and k''_2 given in the text. The circles denote experimental points.

k''_2 obtained from the respective intercepts and slopes of the least squares plots of k_{obs} *vs.* $[Na^+]^2$ (eqn. (6)) for each temperature. Application of the Eyring equation to these rate parameters, k°_2 and k''_2, results in two sets of thermodynamic parameters associated with the spontaneous and Na^+ ion catalysed paths which are also listed in Table III. It is worth mentioning that these activation parameters are composite magnitude since they include the energetics of ion pair formation constants. The lower value of $\Delta H^{\neq}$ for the sodium ion catalysed path compared to that obtained for the uncatalysed path might be explained by assuming that this cation does not act in a simple Coulomb type of interaction, which should have higher $\Delta H^{\neq}$ values, but acts as a catalyst for the reorientation of the outersphere in the transition state [16]. The less positive $\Delta S''_2{}^{\neq}$ value with respect to $\Delta S^\circ_2{}^{\neq}$ is in conformity with a mechanism involving a pronounced participation of the reactants (with a third species) in the transition state which has already been modelled.

Conclusion from Redox Potential Data

The redox potential value (E°_{HCOOH}) of HCOOH is −0.14 V [25]. We have calculated the $E^\circ_{HCOO^-}$ (= −0.25 V) value with the help of the known value [15] of the dissociation constant of formic acid following the standard procedure [26]. The fact that the reaction with formic acid is much slower than that with formate ion is ascribed to the more negative potential value of carboxylate ion compared to the carboxylic acid.

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