# Kinetics of the Oxidation of Formic Acid by Aquacobalt(III) Ions in Aqueous Perchlorate Media

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The rate of oxidation of formic acid by  $C_{aq}^{III}$  has been measured in aqueous perchlorate media over a wide range of conditions using conventional and stopped-flow spectrophotometry. The order in [Co<sup>III</sup>] is unity and the order in [HCOOH] lies between zero and unity; the rate decreases with increasing acidity in a complex manner. The mechanism is resolved into two rate determining processes, each involving an intermediate Co<sup>III</sup>-HCOOH complex. These two complexes have an acid-base relationship involving two protons. Values for  $\Delta H^*$  and  $\Delta S^*$  together with the ratio of rates of oxidation of HCOOH and DCOOH are compared for a range of oxidizing ions.

The kinetics of the oxidation of formic acid have been investigated for a range of ionic oxidant species in aqueous perchlorate media, notably  $MnO_4^{-}$ , <sup>1</sup> $TI^{III}$ , <sup>1</sup> $Hg^{II}$ , <sup>1</sup> $Hg^{I}$ , <sup>1</sup> $Hg^{I}$ , <sup>1</sup> $Ce^{IV}$ , <sup>2</sup> $Mn^{III}$ , <sup>3</sup> $Np^{VII}$  <sup>4</sup> and  $Ag^{II}$ . <sup>5</sup> A common feature is that all are retarded by increasing acidity, except for  $Ce^{IV}$  where the rate increases with increasing acidity. For  $Co^{III}$ , the detailed kinetics have been studied <sup>6</sup> in aqueous sulphate media where the cation exists as a sulphatocobalt(III) complex: <sup>7</sup> the reaction is first order in [Co<sup>III</sup>] and first order in [HCOOH] and the variation with acidity is expressed by rate =  $k'_1 + k'_2[H^+]^{-1}$ .<sup>6</sup> Kemp and Waters <sup>8</sup> have published a few rate measurements with Co<sup>III</sup> in aqueous perchlorate media and they pointed out that the rate is also drecreased by increasing acidity. In this paper, a detailed kinetic study of the oxidation of HCOOH by Co<sup>III</sup> in aqueous perchlorate media is reported.

### EXPERIMENTAL

### MATERIALS

 $Co_{aq}^{II}$  was prepared by anodic oxidation of  $Co_{aq}^{II}$  in aqueous perchloric acid.<sup>9</sup>  $Co_{aq}^{II}$  was prepared by the double decomposition of solutions of AnalaR cobalt (II) sulphate and AnalaR barium perchlorate with removal of the precipitate of BaSO<sub>4</sub> by filtration through Whatman no. 42 paper. Solutions of sodium perchlorate were prepared by the neutralization of AnalaR perchloric acid with AnalaR sodium carbonate followed by boiling and filtration through Whatman no. 42 paper. Solutions of AnalaR FeSO<sub>4</sub>. 7H<sub>2</sub>O and AnalaR barium perchlorate followed by filtration through Whatman no. 42 paper. Water was distilled once in an all-glass still. AnalaR perchloric acid was used.

#### PROCEDURE

[Co<sup>III</sup>] were determined spectrophotometrically at 260 nm by sampling into solutions containing Fe<sup>II</sup>:  $\varepsilon = 2.88 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> for Fe<sup>III</sup><sub>aq</sub> at 260 nm.<sup>10</sup> Rates of disappearance of [Co<sup>III</sup>] were followed by monitoring changes in optical density at 270 nm in the

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thermostatted cell compartment of a Unicam SP500 spectrophotometer for temperatures in the range 2.9-20°C and at 605 nm using a Durrum-Gibson stopped-flow spectrophotometer for 40.1°C; initial  $[Co^{III}] \approx 1 \times 10^{-3}$  mol dm<sup>-3</sup>. In the latter case, reaction traces were photographed on the storage screen of a Tektronix oscilloscope. Constant temperature was obtained by the circulation of water from a thermostat or of a water+ethanol mixture from a cryostat, depending on the temperature. Ionic strength was maintained at  $5.00 \text{ mol dm}^{-3}$ by the addition of sodium perchlorate.

### **RESULTS AND DISCUSSION**

#### STOICHIOMETRY

It is generally agreed <sup>1-6</sup> that the overall reaction for the oxidation of formic acid by metal cations  $M^{n+}$  is

$$2M^{n+} + HCOOH \rightarrow 2M^{(n-1)+} + CO_2 + 2H^+$$
 (1)

and this was confirmed for  $M^{n+} = Mn^{III}$  in our laboratory.<sup>3</sup> However, working at 25°C, with initial [Co<sup>III</sup>] > 2 × initial [HCOOH], with the latter being  $3.00 \times 10^{-4}$ mol dm<sup>-3</sup>, the consumption ratio  $|\Delta[Co^{III}]|/|\Delta[HCOOH]|$  was found to lie between 2 and 3. The reaction was sufficiently slow to be left overnight to achieve completion and it was judged that the deviation from eqn (1) arises from the disappearance of [Co<sup>III</sup>] in the oxidation of water.<sup>11-13</sup> To speed up the oxidation of HCOOH, the determination was done at 49°C, when  $|\Delta[Co^{III}]|/|\Delta[HCOOH]|$  rose to 3.3; presumably, the loss of [Co<sup>III</sup>] through the oxidation of water also increases when the temperature is raised. We believe, however, that there can be little doubt that the overall reaction for Co<sup>III</sup> in aqueous perchlorate media conforms to eqn (1), as found <sup>6</sup> for sulphatocobalt (III) ions in aqueous sulphuric acid.



B×[HCOOH]/dm<sup>3</sup> mol<sup>-1</sup>

FIG. 1.—Plots of  $k_0^{-1}$  against [HCOOH]<sup>-1</sup> for 1.25 mol dm<sup>-3</sup> HClO<sub>4</sub> at ionic strength = 5.00 mol dm<sup>-3</sup>.  $\odot$ , 2.9°C, A = 1.0, B = 1.0;  $\Box$ , 10.8°C, A = 2.0, B = 1.0;  $\triangle$ , 15.2°C, A = 5.0, B = 1.0; ×, 20.0°C, A = 10.0, B = 1.0;  $\forall$ , 25.0°C, A = 20.0, B = 1.0;  $\bullet$ , 30.0°C, A = 20.0, B = 0.4; **I**, 40.1°C, A = 1000.0, B = 10.

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It was found for all conditions that plots of log (optical density) against time gave straight lines, from which it is concluded that the reaction is first order in [Co<sup>III</sup>]. Plots of the pseudo first-order rate constant  $k_0$  against [HCOOH] were not linear, the extent of the deviation from linearity increasing as the acidity decreased. However, plots of  $k_0^{-1}$  against [HCOOH]<sup>-1</sup> at constant acidity are linear; those for [HClO<sub>4</sub>] = 1.25 mol dm<sup>-3</sup> are shown in fig. 1. It is therefore concluded that the order in [HCOOH] lies between zero and one. Values for  $k_0$  determined for all the conditions at ionic strength = 5.00 mol dm<sup>-3</sup> are given in table 1.

Table 1.—Values of the pseudo first-order rate constant  $10^5 k_0(s^{-1})$  with varying [HCOOH] and temperature at a constant ionic strength of 5.00 mol dm<sup>-3</sup>

temp.	[HClO <sub>4</sub> ] $(mol dm^{-3})$	[HCOOH]/mol dm <sup>3</sup>								
70	/mor din -	0.0212	0.0424	0.0635	0.0847	0.106	0.127	0.159	0.212	
2.9	5.00	3.55	6.9	10.1	12.8	16.1	19.6	25.8	33.4	
2.9	4.00	3.20	6.5	9.5	13.0	15.3	17.9	22.5	<b>28.9</b>	
2.9	3.00	3.17	6.8	9.8	13.3	16.6	20.0	24.1	30.0	
2.9	2.00	4.08	7.7	11.8	14.5	18.8	21.9	25.6	34.5	
2.9	1.25	6.04	11.5	17.4	22.0	26.3	31.0	38.4	46.4	
2.9	1.00	7.26	14.4	17 <b>.9</b>	24.4	30.1	36.4	33.7	53	
10.8	5.00	11.7	22.8	33.6	42.4	57	69	83	103	
10.8	4.00	11.9	23.3	32.6	43.4	53		78	94	
10.8	3.00	11.3	23.8	35.2	45.0	56	66	80	103	
10.8	2.00	15.0	27.7	38.0	54	62	<b>89</b>	97	126	
10.8	1.25	19.3	48.7	65	89	101	115	140	185	
10.8	1.00	25.6	39.5	65	87	104	124	130	183	
15.2	5.00	24.4	47.4	65	95	118	145	180	228	
15.2	4.00	24.3	48.0	72	94	120	143	163	225	
15.2	3.00	24.3	44.9	67	92	117	136	160	236	
15.2	2.00	27.9	56	85	117	140	162	201	252	
15.2	1.25	42.2	80	111	152	184	214	265	354	
15.2	1.00	37.1	86	123	157	188	254	288	409	
20.0	5.00	48.8	96	143	192	250	302	351	242	
20.0	4.00	52	<b>9</b> 8	130	190	243	270	363	409	
20.0	3.00	53	106	161	203	266	313	384	469	
20.0	2.00	67	106	186	265	332	384	475	620	
20.0	1.25	85	175	258	318	427	465	570	650	
20.0	1.00	98	192	305	372	485	580	660	800	
25.0	5.00	105	202	290	392	496	540	640	900	
25.0	4.00	108	199	285	371	459	••	690	840	
25.0	3.00	113	204	304	382	441		670	8 <b>90</b>	
25.0	2.00	136	229	364	461	559		800	1030	
25.0	1.50	163	314	466	625	740	860	1030	1270	
25.0	1.25	192	345	520	670	830	980	1160	1420	
25.0	1.00	233	379	570	750	880	1020	1150	1410	

			VALUES (	OF $10^2 k_0$ (s <sup>-</sup>	-1)			
temp.	[HClO <sub>4</sub> ]			[HCO	OH]/mol d	m <sup>-3</sup>		
70	/mor ant	0.200	0.300	0.400	0.500	0.600	0.800	1.00
40.1	5.00	5.7		6.5		9.2	16.2	19.6
40.1	4.00		6.0	7.9	9.2	11.3	15.5	
40.1	3.00	5.0		7.8		11.5	13.6	17.1
40.1	2.00	5.7		10.7	_	12.8	17.4	21.9
40.1	1.25	8.7		14.5		17.7	21.7	22.7
40.1	1.00	10.4		16.6		17.5	23.3	27.0

# TABLE 1 (continued)

## VALUES OF $10^{3}k_{0}(s^{-1})$

[HClO <sub>4</sub> ]					[HCO	OH]/mo	l dm-3						
/mol dm <sup>-3</sup>	0.0106	0.0212	0.0317	0.0424	0.0530	0.0635	0.0742	0.0847	0.0954	0.106	0.127	0.159	0.221
5.00		2.22		4.22		6.20		7.7		10.0	12.2	13.6	18.1
4.00	1.13	2.22	3.16	3.89	5.00	5.60	6.5	7.8	8.2	8.8			
3.00	1.20	2.28	3,33	4.25	5.00	5.70	7.1	8.2	9.6	10.5			
2.00	1.51	2.88	3.75	4.83	5.90	6.90	8.0	9.4	11.0	11.6	13.4		_
1.25	2.08	3,96	5.30	6.70	8.40	9.60	11.0	11.6	12.6	14.3	15.8	-	
1.00	2,46	4.51	6.20	7.00	9.70	11.3	13.9	14.5		16.4	-	-	-
	[HClO <sub>4</sub> ] /mol dm <sup>-3</sup> 5.00 4.00 3.00 2.00 1.25 1.00	[HClO4]           /mol dm <sup>-3</sup> 0.0106           5.00            4.00         1.13           3.00         1.20           2.00         1.51           1.25         2.08           1.00         2.46	[HCIO4]         /mol dm <sup>-3</sup> 0.0106       0.0212         5.00        2.22         4.00       1.13       2.22         3.00       1.20       2.28         2.00       1.51       2.88         1.25       2.08       3.96         1.00       2.46       4.51	[HCIO4]         /mol dm <sup>-3</sup> 0.0106       0.0212       0.0317         5.00        2.22          4.00       1.13       2.22       3.16         3.00       1.20       2.28       3.33         2.00       1.51       2.88       3.75         1.25       2.08       3.96       5.30         1.00       2.46       4.51       6.20	[HCIO4]         /mol dm <sup>-3</sup> 0.0106       0.0212       0.0317       0.0424         5.00        2.22        4.22         4.00       1.13       2.22       3.16       3.89         3.00       1.20       2.28       3.33       4.25         2.00       1.51       2.88       3.75       4.83         1.25       2.08       3.96       5.30       6.70         1.00       2.46       4.51       6.20       7.00	[HClO4]         [HCO           /mol dm <sup>-3</sup> 0.0106         0.0212         0.0317         0.0424         0.0530           5.00          2.22          4.22            4.00         1.13         2.22         3.16         3.89         5.00           3.00         1.20         2.28         3.33         4.25         5.00           2.00         1.51         2.88         3.75         4.83         5.90           1.25         2.08         3.96         5.30         6.70         8.40           1.00         2.46         4.51         6.20         7.00         9.70	[HCIO4]         [HCOOH]/mol           /mol dm <sup>-3</sup> 0.0106         0.0212         0.0317         0.0424         0.0530         0.0635           5.00          2.22          4.22          6.20           4.00         1.13         2.22         3.16         3.89         5.00         5.60           3.00         1.20         2.28         3.33         4.25         5.00         5.70           2.00         1.51         2.88         3.75         4.83         5.90         6.90           1.25         2.08         3.96         5.30         6.70         8.40         9.60           1.00         2.46         4.51         6.20         7.00         9.70         11.3	$[HCIO_4] \qquad [HCOOH]/mol dm^{-3} \\ (mol dm^{-3} 0.0106 0.0212 0.0317 0.0424 0.0530 0.0635 0.0742 \\ \hline \\ 5.00 & 2.22 & 4.22 & 6.20 & \\ 4.00 1.13 2.22 3.16 3.89 5.00 5.60 6.5 \\ 3.00 1.20 2.28 3.33 4.25 5.00 5.70 7.1 \\ 2.00 1.51 2.88 3.75 4.83 5.90 6.90 8.0 \\ 1.25 2.08 3.96 5.30 6.70 8.40 9.60 11.0 \\ 1.00 2.46 4.51 6.20 7.00 9.70 11.3 13.9 \\ \end{tabular}$	$[HCIO_4] \qquad [HCOOH]/mol dm^{-3} \\ /mol dm^{-3} 0.0106 0.0212 0.0317 0.0424 0.0530 0.0635 0.0742 0.0847 \\ \hline \\ 5.00 - 2.22 - 4.22 - 6.20 - 7.7 \\ 4.00 1.13 2.22 3.16 3.89 5.00 5.60 6.5 7.8 \\ 3.00 1.20 2.28 3.33 4.25 5.00 5.70 7.1 8.2 \\ 2.00 1.51 2.88 3.75 4.83 5.90 6.90 8.0 9.4 \\ 1.25 2.08 3.96 5.30 6.70 8.40 9.60 11.0 11.6 \\ 1.00 2.46 4.51 6.20 7.00 9.70 11.3 13.9 14.5 \\ \hline \end{tabular}$	$[HClO4] \\ [HClO4] \\ \hline \hline \\ \hline \hline [HClo4] \hline \hline \hline \\ \hline \hline \\ \hline \hline \\ \hline \hline \hline \hline \\ \hline \hline \hline \hline $	$[HClO_4] = \begin{bmatrix} HCOOH \end{bmatrix} / mol dm^{-3} \\ 0.0106 & 0.0212 & 0.0317 & 0.0424 & 0.0530 & 0.0635 & 0.0742 & 0.0847 & 0.0954 & 0.106 \\ \hline \\ 5.00 & & 2.22 & & 4.22 & & 6.20 & & 7.7 & & 10.0 \\ 4.00 & 1.13 & 2.22 & 3.16 & 3.89 & 5.00 & 5.60 & 6.5 & 7.8 & 8.2 & 8.8 \\ 3.00 & 1.20 & 2.28 & 3.33 & 4.25 & 5.00 & 5.70 & 7.1 & 8.2 & 9.6 & 10.5 \\ 2.00 & 1.51 & 2.88 & 3.75 & 4.83 & 5.90 & 6.90 & 8.0 & 9.4 & 11.0 & 11.6 \\ 1.25 & 2.08 & 3.96 & 5.30 & 6.70 & 8.40 & 9.60 & 11.0 & 11.6 & 12.6 & 14.3 \\ 1.00 & 2.46 & 4.51 & 6.20 & 7.00 & 9.70 & 11.3 & 13.9 & 14.5 & & 16.4 \\ \hline \end{tabular}$	$[HCOOH]/mol dm^{-3} \\ (mol dm^{-3} 0.0106 0.0212 0.0317 0.0424 0.0530 0.0635 0.0742 0.0847 0.0954 0.106 0.127 \\ \hline \\ \hline \\ 5.00 - 2.22 - 4.22 - 6.20 - 7.7 - 10.0 12.2 \\ 4.00 1.13 2.22 3.16 3.89 5.00 5.60 6.5 7.8 8.2 8.8 - 3.00 1.20 2.28 3.33 4.25 5.00 5.70 7.1 8.2 9.6 10.5 - 2.00 1.51 2.88 3.75 4.83 5.90 6.90 8.0 9.4 11.0 11.6 13.4 \\ 1.25 2.08 3.96 5.30 6.70 8.40 9.60 11.0 11.6 12.6 14.3 15.8 \\ 1.00 2.46 4.51 6.20 7.00 9.70 11.3 13.9 14.5 - 16.4 - \\ \hline \\ \end{tabular}$	$[HCOO4] \qquad [HCOO4]/mol dm^{-3} \\ (mol dm^{-3} 0.0106 0.0212 0.0317 0.0424 0.0530 0.0635 0.0742 0.0847 0.0954 0.106 0.127 0.159 \\ \hline \\ 5.00 - 2.22 - 4.22 - 6.20 - 7.7 - 10.0 12.2 13.6 \\ 4.00 1.13 2.22 3.16 3.89 5.00 5.60 6.5 7.8 8.2 8.8 \\ 3.00 1.20 2.28 3.33 4.25 5.00 5.70 7.1 8.2 9.6 10.5 \\ 2.00 1.51 2.88 3.75 4.83 5.90 6.90 8.0 9.4 11.0 11.6 13.4 - \\ 1.25 2.08 3.96 5.30 6.70 8.40 9.60 11.0 11.6 12.6 14.3 15.8 - \\ 1.00 2.46 4.51 6.20 7.00 9.70 11.3 13.9 14.5 - 16.4 \\ \hline \\ \end{tabular}$

## VARIATION OF RATE WITH [HClO<sub>4</sub>]

In general it was found that the rate of the oxidation increased with decreasing acidity. Values for the slope and intercepts for the linear plots of  $k_0^{-1}$  against [HCOOH]<sup>-1</sup> determined by the least-squares procedure are given in table 2 and 3.

Table 2.—Values of the slopes (dm<sup>-3</sup> mol s) of the plots of  $k_0^{-1}$  against [HCOOH]<sup>-1</sup> for varying acidity and temperature

$\frac{\text{temp}/^{\circ}\text{C}}{[\text{HClO}_4]}$ /mol dm <sup>-3</sup>	2.9	10.8	15.2	20.0	25.0	30.0	40.1
5.00	596	179	86	43.3	19.8	9.28	3.42
4.00	655	174	86	40.1	19.1	9.12	4.78
3.00	667	186	87	39.7	18.0	8.62	3.46
2.00	509	139	77	31.7	15.3	6.76	3.14
1.50	<u> </u>			*	12.6		
1.25	339	107	49	24.4	10.7	4.81	1.80
1.00	275	81	49	21.2	8.6	4.07	1.41

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temp/°C [HCIO <sub>4</sub> ] /mol dm <sup>-3</sup>	2.9	10.8	15.2	20.0	25.0	30.0	<b>40.</b> ]
5.00	490	122	69	8.6	24	15	3.5
4.00	248	241	46	58	38	26	0.83
3.00	-260	18.5	73	9.7	45	26	3.0
2.00	640	214	81	29	35	32	1.8
1.50					17		
1.25	530	- 72	81	19	21	29	2.5
1.00	800	244	37	13	35	27	2.6

**TABLE 3.**—VALUES OF THE INTERCEPTS (S) OF THE PLOTS OF  $k_0^{-1}$  AGAINST [HCOOH]<sup>-1</sup> FOR VARYING ACIDITY AND TEMPERATURE

#### MECHANISM OF THE OXIDATION

The curved plots found for  $k_0$  against [HCOOH] with the linear variation for  $k_0^{-1}$  against [HCOOH]<sup>-1</sup> strongly suggests that an intermediate complex is involved, although no evidence was found for this on the stopped-flow traces obtained at 40.1°C. The following equilibria are likely to exist <sup>3</sup>. 9. 12, 14, 15</sup> at these high acidities

$$\operatorname{Co}_{aq}^{III} \stackrel{K_{h}}{\approx} \operatorname{Co}_{aq}^{III} O H^{-} + H_{aq}^{+}$$

$$(2)$$

$$\operatorname{Co}_{aq}^{III} + \operatorname{HCOOH} \rightleftharpoons \operatorname{Co}^{III} \operatorname{HCOOH}_{aq}$$
(3)

$$Co^{111}HCOOH_{aq} \rightleftharpoons Co^{111}HCOO_{aq}^{-} + H_{aq}^{+}$$
(4)

with the rate determining steps

$$Co^{III}HCOOH_{aq} \xrightarrow{k_1} Co^{II}_{aq} + COOH + H^+_{aq}$$
(5)

$$Co^{III}HCOO_{aq}^{-} \xrightarrow{\kappa_{2}} Co_{aq}^{II} + \cdot COOH$$
 (6)

followed by the very rapid step

$$\operatorname{Co}_{\operatorname{aq}}^{\operatorname{III}} + \operatorname{COOH} \to \operatorname{Co}_{\operatorname{aq}}^{\operatorname{II}} + \operatorname{CO}_2 + \operatorname{H}_{\operatorname{aq}}^+.$$
(7)

Using reactions (2)-(7) and assuming that the pre-equilibria (2)-(4) are rapidly established compared with reactions (5) and (6), eqn (8) accounts for the linear relationships between  $k_0^{-1}$  and [HCOOH]<sup>-1</sup>, where [HCOOH]<sub>T</sub> = the total added concentration of formic acid and  $h = [H_{ac}^+] = [HCIO_4]$ .

$$\frac{1}{k_0} = \frac{(1+K_hh^{-1})}{2\beta_1(k_1+k_2K_1h^{-1})[\text{HCOOH}]_{\text{T}}} + \frac{(1+K_1h^{-1})}{2(k_1+k_2K_1h^{-1})}$$
(8)

The slopes, S, of the plots of  $k_0^{-1}$  against [HCOOH]<sub>T</sub><sup>-1</sup> will be given by

$$0.5(1 + K_{\rm h}h^{-1})S^{-1} = \beta_1(k_1 + k_2K_1h^{-1}) \tag{9}$$

and the l.h.s. of eqn (9) should vary linearly with  $h^{-1}$ . However, such plots were found to be curved, but plots of  $0.5(1 + K_h h^{-1})S^{-1}$  against  $h^{-2}$  are linear. These plots are compared for 25°C in fig. 2. The plots of  $0.5(1 + K_h h^{-1})$  against  $h^{-2}$  for all temperatures are given in fig. 3. The values of  $K_h$  used were calculated from the

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values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  for reaction (2) given by Sutcliffe and Weber.<sup>14</sup> This variation can be accounted for if the reactions (10) and (11)

$$\operatorname{Co}^{III}\operatorname{HCOOH}_{aq} \stackrel{K_2}{\approx} \operatorname{Co}^{III}(\operatorname{OH}^-)\operatorname{HCOO}_{aq}^- + 2\operatorname{H}^+$$
 (10)

$$\operatorname{Co}^{III}(OH^{-})\operatorname{HCOO}_{aq}^{-} \xrightarrow{\kappa_{3}} \operatorname{Co}_{aq}^{II} + \operatorname{cOO}^{-} + \operatorname{H}_{2}O$$
(11)

operate, together with reactions (2), (3), (5) and (7), with reactions (5) and (11) rate determining. Eqn (12) and (13) result from these reactions

$$\frac{1}{k_0} = \frac{1 + K_h h^{-1}}{2\beta_1 (k_1 + k_3 K_2 h^{-2}) [\text{HCOOH}]_T} + \frac{1 + K_2 h^{-1}}{2(k_1 + k_3 K_2 h^{-2})}$$
(12)

$$0.5(1+K_{\rm h}h^{-1})S^{-1} = \beta_1(k_1+k_3K_2h^{-2}). \tag{13}$$

The intercepts, I, of the plots of  $k_0^{-1}$  against [HCOOH]<sub>T</sub><sup>-1</sup> will be given by eqn (14)

$$I(1+K_{\rm h}h^{-1})S^{-1} = \beta_1(1+K_2h^{-2}) \tag{14}$$

but table 3 and fig. 1 show that these values of I are too small and erratic for eqn (14) to be tested. There is, of course, an alternative pathway to reactions (10) and (11), namely,

$$\operatorname{Co}^{III}\operatorname{HCOOH}_{aq} \rightleftharpoons \operatorname{Co}(\operatorname{OH}^{-})_{2}\operatorname{HCOOH}_{aq} + 2\operatorname{H}_{aq}^{+}$$
 (15)

$$\operatorname{Co}^{111}(OH^{-})_{2}HCOOH_{aq} \xrightarrow{k_{3}} \operatorname{Co}_{aq}^{11} + H_{2}O + \bullet COOH$$
(16)

but reactions (15) and (16) are kinetically indistinguishable from reactions (10) and (11).



FIG. 2.—Plots of 0.5  $(1 + K_h h^{-1})S^{-1}$  against  $h^{-1}(\odot)$  and  $h^{-2}(\Box)$  for ionic strength = 5.00 mol dm<sup>-1</sup> at 25°C.

The values of the slopes and intercepts of the plots of 0.5  $(1 + K_h h^{-1})S^{-1}$  against  $h^{-2}$  found by the least-squares procedure are collected in table 4. Plots of  $\log \beta_1 k_3 K_2$  and of  $\log \beta_1 k_1$  against the reciprocal of absolute temperature are linear. From these plots it is found, using the least-squares procedure, that for  $\beta_1 k_1$ ,  $\Delta H^* = 99 \pm 4 \text{ kJ mol}^{-1}$  and  $\Delta S^* = 53 \pm 14 \text{ J K}^{-1} \text{ mol}^{-1}$  and for  $\beta_1 k_3 K_2$ ,  $\Delta H^* = 106 \pm 4 \text{ kJ mol}^{-1}$  and  $\Delta S^* = 80 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ .



FIG. 3.—Plots of 0.5  $(1 + K_h h^{-1})S^{-1}$  against  $h^{-2}$  at ionic strength = 5.00 mol dm<sup>-3</sup>.  $\bigcirc$ , 2.9°C, A = 1000;  $\bigcirc$ , 10.8°C, A = 200;  $\triangle$ , 15.2°C, A = 100;  $\times$ , 20.0°C, A = 20;  $\bigcirc$ , 30.0°C, A = 10;  $\blacksquare$ , 40.1°C, A = 2.

#### COMPARISON WITH OXIDATION BY OTHER CATIONS

These results contrast markedly with those for the oxidation of formic acid by sulphatocobalt(III) ions in aqueous sulphuric acid,<sup>6</sup> where no intermediate was detected kinetically and the rate varied with acidity according to rate  $= k'_1 + k'_2 h^{-1}$ . Kemp and Waters<sup>8</sup> reported for a few results at 25°C for aquacobalt (III) ions in aqueous perchloric acid that the variation of rate with acidity is of the same form as found by Bawn and White for sulphatocobalt(III) ions, but quantitatively these few data at 25°C fit the equation rate  $= k'_1 + k'_3 h^{-2}$ , analogous to the results reported in this paper. However, Kemp and Waters' data are not sufficiently extensive to test the above mechanism.

temp./°C	$\beta_1 k_3 K_2 \times 10^3$	$\beta_1 k_1 \times 10^3$	
2.9	1.13	0.71	
10.8	3.57	2.56	
15.2	5.5	5.5	
20.0	12.8	11.7	
25.0	35.3	24.1	
30.0	77	52	
40.1	256	112	

TABLE 4.—VALUES OF  $\beta_1 k_3 K_2/dm^{-3} \mod s^{-1}$  and  $\beta_1 k_1/dm^3 \mod^{-1} s^{-1}$  taken from the slopes and intercepts of plots of  $0.5(1 + K_h h^{-1})$  against  $h^{-2}$ 

Of the other oxidizing species in aqueous perchlorate media,  $MnO_4^{-1}$  follows rate  $= k'_1 + k'_2 h^{-1}$ , whereas  $Hg_{aq}^{II}$ ,  $Hg_{aq}^{I}$  and  $Tl_{aq}^{III}$  follow rate  $= k_2 h^{-1}$ ; an intermediate complex was detected only for  $Tl^{III}$ . The oxidation by  $Mn_{aq}^{III}$  proceeds <sup>3</sup>

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*via* the analogues of reactions (5) and (6) above  $40^{\circ}$ C and *via* the analogues of reactions (5) and (11) below  $25^{\circ}$ C; the oxidation by  $Ce_{aq}^{IV}$  proceeds <sup>2</sup> *via* the analogues of reactions (5) and (6) in the temperature range 24-47°C. The retardation by acidity of the rate of oxidation by Ag<sup>II</sup> follows a complex order, with hydrolytic species of Ag<sup>II</sup> and Ag<sup>III</sup> involved;<sup>5</sup> no intermediate complexes were detected; however, in aqueous nitrate media <sup>16</sup> the oxidation by Ag<sup>II</sup> appears to follow a simpler mechanism.

**Table 5.** — Values for various oxidants with formic acid of overall enthalpies  $(kJ \text{ mol}^{-1})$  and entropies  $(J \text{ K}^{-1} \text{ mol}^{-1})$  of activation for  $k'_1$  and  $k'_2$  in rate  $= k'_1 + k'_2 h^{-1}$ and for  $k'_3$  for overall reactions (11) or (16); values of rate constants for oxidation of HCOOH and DCOOH

oxidant	$E^{\circ}/V$	added anion	reaction	Δ <i>H</i> *	ΔS*	k <sub>H</sub> /k <sub>D</sub>
MnO <sub>4</sub>	0.57	ClO <sub>4</sub>	k'1	67	- 80	1.0
MnO <sub>4</sub>	0.57	$ClO_4^-$	k'2	50	- 59	7.0
Hg <sup>2+</sup>	0.907	$ClO_4^-$	k'2	84	+13	3.4
$Hg_{2}^{2+}$	0.792	ClO <sub>4</sub>	$k'_2$	88	zero	3.9
Tl <sup>3+</sup>	1.26-0.65	C10_	$k'_2$	109	+88	3.4
Сош	≈1.8	$SO_4^{2-}$	$k'_1$	110	+88	<u> </u>
Co <sup>III</sup>	$\approx 1.8$	$SO_4^{2-}$	$k_2'$	88	+97	
Сош	1.95	$ClO_4^-$	$k'_1$	99	+ 53	1.4
Сош	1.95	ClO <sub>4</sub>	$k'_3$	106	+80	1.8
Mn <sup>III</sup>	1.49	ClO <sub>4</sub>	$k_1^{\tilde{\prime}}$	<b>9</b> 6	-8	
Mn <sup>III</sup>	1.49	ClO <sub>4</sub>	$k'_2$	126	+92	
Mn <sup>III</sup>	1.49	ClO <sub>4</sub>	$k'_3$	44	- 190	
Np <sup>vII</sup>	>2.0	ClO <sub>4</sub>	$k_1'$	25	-171	10
	>2.0	$ClO_{4}^{-}$	$k_{2}$	42	-130	10

Table 5 shows a comparison of data for the overall oxidation processes for a range of cations in aqueous perchlorate media, together with that for Co<sup>III</sup> in aqueous sulphate media. There seems to be no real correlation of  $\Delta H^*$  and  $\Delta S^*$  with electrode potential for the cation, probably reflecting differences in the detailed mechanism. Only with  $TI_{aq}^{III}$ ,  $Co_{aq}^{II}$  and  $Mn_{aq}^{III}$  is the reaction known to go through an intermediate complex. The oxidation by  $Ce_{aq}^{IV}$  also proceeds *via* intermediate complexes, but  $\Delta H^*$  and  $\Delta S^*$  are only available for a complex function involving the rate constant and an acid-base equilibrium constant.<sup>2</sup> Another indication of differences in the detailed mechanisms is indicated by the wide range in values for the isotope effects,  $k_{\rm H}/k_{\rm D}$ , for the comparison of HCOOH with DCOOH : the values for  $Co_{\rm aq}^{III}$  is calculated from the slopes and intercepts of the plots of rate constant against  $[H^+]^{-2}$  using Kemp and Waters' data.<sup>8</sup> Clearly, for MnO<sub>4</sub><sup>-</sup> any change in the C—H bond has little influence on the transition state and possibly also for  $Co_{\rm aq}^{III}$ , *i.e.*, for these, electron transfer is probably controlling: for the remainder, the breakage of the C—H bond does contribute to the transition state.

It is only possible to compare in detail reactions having the same kinetic form, *i.e.*, the overall rate constant  $k'_1$  for reaction (5) for  $Mn_{aq}^{III}$  and  $Co_{aq}^{III}$  with  $k'_1$  for  $Np_{aq}^{VII}$  in rate  $= k'_1 + k'_2 h^{-1}$  and the overall  $k'_3$  for reaction (11) involving  $Mn_{aq}^{III}$  and  $Co_{aq}^{III}$ .

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Although  $k'_3(dm^{-3} \text{ mol s}^{-1})$  at 25°C is in the same order as the redox potentials  $Co_{ard}^{III}(3.54 \times 10^{-3}) > Mn_{aq}^{III}(3.41 \times 10^{-5})$ , the overall  $\Delta H^*$  for  $Co_{ard}^{III} > \Delta H^*$  for  $Mn_{aq}^{III}$  (table 5); the order in rates results from the large negative  $\Delta S^*$  for  $Mn_{aq}^{III}$  compared with a large positive  $\Delta S^*$  for  $Co_{aq}^{III}$ . Likewise,  $k'_1(dm^3 mol^{-1} s^{-1})$  at 25°C is in the same order as the redox potentials,  $Np_{aq}^{VII}(0.40) > Co^{III}(2.41 \times 10^{-2}) > Mn_{aq}^{III}(7.2 \times 10^{-5})$ , but the order for overall  $\Delta H^*$  is  $Np_{aq}^{VII} > Mn_{aq}^{III} > Co_{aq}^{III}$ , with  $Co_{aq}^{III}$  again displaced from the expected order. This can be compared with similar series with other oxidizable ligands, where  $Co_{aq}^{III}$  appears to be displaced from the order expected on the  $E^\circ$  values.<sup>15</sup> With HCOOH and  $k'_1$ , only  $Co_{aq}^{III}$  has a positive values for  $\Delta S^*$ . These large positive  $\Delta S^*$  for  $k'_1$  and  $k'_3$  for  $Co_{aq}^{III}$  with HCOOH and also for other oxidizable ligands with  $Co_{aq}^{III}$  can be explained if two electron transfers are involved with dimeric  $Co_{aq}^{III}$  9, <sup>11-15</sup> in aqueous perchloric acid and probably also for  $Co^{III}$  in aqueous sulphuric acid:<sup>11</sup> the consequential large loss of charge in the transition state will result in a large loss of restriction on the solvent molecules with a concomitant large positive  $\Delta S^*$ . If  $Co_{aq}^{III} = dimer ^{9, 11-15}$  in the above mechanisms in aqueous perchlorate media, then  $\Delta S^*$  becomes  $59 \pm 14 \text{ J K}^{-1}$  mol<sup>-1</sup> for  $\beta_1 k_1 \text{ and} 86 \pm 6 \text{ J K}^{-1}$  mol<sup>-1</sup> for  $\beta_1 k_3 K_2$ ; moreover, with a dimer reactions (15) and (16) become more likely at alternatives. For monomeric  $Co_{aq}^{III}$  presumably the arrangement in the transition states are similar to those described for Mn\_{aq}^{III}, with the order in  $\Delta S^*$  arising from the changes in the relative positions of the atoms in going from the initial to the transition state.

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