Catalysis by Metal Cations. Part III.[1] Kinetics of Elimination of Chloride Ion from *cis*-Chlorobis(ethylenediamine)glycinato-*N*-cobalt(III)

By **H. M. Comley** and **W. C. E. Higginson**,* Department of Chemistry, The University, Hull HU6 7RX

The pH-dependence of the rate of loss of chloride ion from *cis*-chlorobis(ethylenediamine)glycinato-*N*-cobalt(III) indicates weak S_N2 character involving participation of the free carboxylate group of the unidentate glycinato-ligand. Weakly basic anions mildly assist the reaction, the effect increasing with the base strength of the anion. At pH 5 the reaction is greatly assisted by Pb^{2+} ions and shows stronger S_N2 character.

Loss of the chloride ligand from the quinquedentate complex anion chloro(ethylenediaminetriacetatoacetate)-cobaltate(III) to give sexidentate ethylenediaminetetra-acetatocobaltate(III) is assisted by metal cations, the effect of these being highly pH-dependent. In contrast, the reaction rate shows only a small dependence on pH in the absence of such cations. Complex formation between the active cations and the substrate has been shown to occur, and the reaction involves an internal S_N2 displacement of the chloride ligand by the entering carboxylate group.[1,2] Similar studies have been made with dichloro-(ethylenediaminediacetate)platinate(II).[3]

The object of the present work was to investigate the behaviour of a positively charged cobalt(III) complex which undergoes a similar chelation reaction. We found that the complex *cis*-chlorobis(ethylenediamine)glycinato-*N*-cobalt(III) was suitable. This complex was first prepared by Alexander and Busch[4] who observed its slow chelation in solution to give bis(ethylenediamine-glycinato-*O*,*N*-cobalt(III) with loss of the chloride ligand.

RESULTS

The visible spectra of the *cis*-chlorobis(ethylenediamine)-glycinato-*N*-cobalt(III) complex and its conjugate acid *cis*-chlorobis(ethylenediamine)glycine-*N*-cobalt(III) are very similar[4] and differ considerably from that of the chloride-elimination product. Hence the reaction was followed spectrophotometrically, 550 nm being a suitable wavelength. Plots of $\log(D_t - D_\infty)$ against time t were linear (D_t and D_∞ represent the optical density at time t and at the end of the reaction respectively) showing the reaction to be first order in the glycinato-*N* complex. All kinetic experiments were carried out at 45·0 °C and the ionic strength was made 1·00M by addition of sodium perchlorate solution, except where otherwise stated. Readings were normally taken throughout the first 75% of the reaction.

Preliminary results showed that in the region pH 0·3—1·0 the reaction rate constant, $k_{obs} = -2{\cdot}3d[\log(D_t - D_\infty)]/dt$, was little affected by change in pH. However, as pH values were further increased there was a corresponding increase in k_{obs} until, at pH 4·5—5·0, the value of k_{obs} was approximately double that at pH 1·0. This behaviour suggested that the glycinato-*N* complex reacts twice as quickly as its conjugated acid since the pK of the latter is *ca.* 2·1.[4] However, it was found that k_{obs} was also affected by the buffer concentration and so several groups of experiments, summarised in Table 1, were undertaken with varying buffer

TABLE 1

Effect of buffer base concentration, [A], on the rate constant k_{obs}

pH	[A]/M	10^5k_{obs}/s^{-1}	pH	[A]/M	10^5k_{obs}/s^{-1}
Acetate; $r \simeq 0{\cdot}8$			Chloroacetate; $r \simeq 1{\cdot}4$		
4·40	0·019	1·96	2·79	0·057	1·64
4·49	0·043	1·98	2·80	0·087	1·67
4·41	0·058	2·03	2·80	0·118	1·71
4·51	0·078	2·03	2·81	0·151	1·75
4·52	0·090	2·05	2·83	0·182	1·78
4·52	0·101	2·03			
4·46	0·104	2·08	$r \simeq 7$		
4·48	0·128	2·09	3·47	0·069	1·82
4·58	0·133	2·09	3·49	0·087	1·84
			3·51	0·133	1·90
$r \simeq 3$			3·50	0·175	1·96
5·04	0·037	2·13	3·52	0·220	2·05
5·12	0·077	2·25	3·53	0·269	2·08
5·15	0·116	2·37			
5·30	0·145	2·39	Monohydrogen phosphate; $r \simeq 1$		
5·12	0·153	2·43			
5·32	0·188	2·43	7·10	0·040	3·05
5·22	0·201	2·48	7·12	0·050	3·30
5·31	0·229	2·47	7·13	0·075	3·54
5·17	0·241	2·57	7·15	0·100	3·86
			7·16	0·125	4·26
			7·18	0·150	4·51

r = [Buffer base]/[Buffer acid].

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[1] Part II, S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1969, 1164.

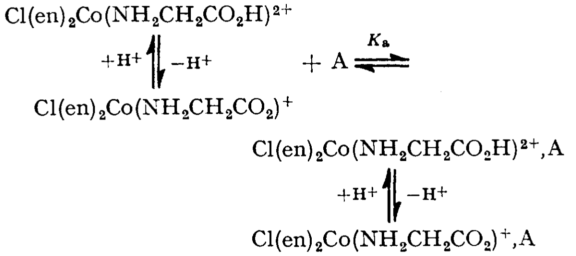
[2] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1963, 2788.

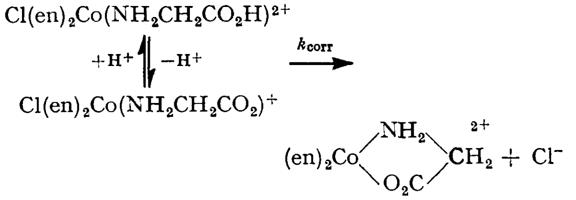
[3] S. P. Tanner, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1967, **6**, 1089.

[4] M. D. Alexander and D. H. Busch, *Inorg. Chem.*, 1966, **5**, 1590.

concentrations at an approximately constant pH. For chloroacetate and hydrogen phosphate (HPO_4^{2-}) the plots of k_{obs} against buffer concentration were linear, but with acetate plots were curved, suggesting a considerable degree of association between acetate ion and the substrate.

We can describe the effect of the buffer base (A) at a given pH by the following reaction scheme:


(1)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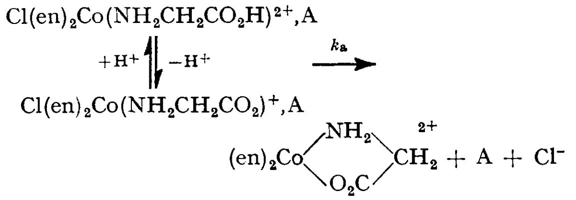

(3)

From this we deduce equation (4). If K_a[A] is sufficiently

$$k_{obs} = k_{corr} + (k_a - k_{corr})K_a[A]/(1 + K_a[A]) \quad (4)$$

small compared with unity, the plot of k_{obs} against [A] will be linear, equation (5), where $k_b \simeq (k_a - k_{corr})K_a$. Assuming

$$k_{obs} = k_{corr} + k_b[A] \quad (5)$$

ing that the relative standard deviation of each value of k_{obs} in Table 1 is 3·0%, using weighted least-squares procedures, the results in this Table, together with the corresponding values of the standard deviation, can be summarised as shown in Table 2. Values of k_{obs} over a range of pH values are given in Table 3. By using the above equations relating k_{corr} to k_{obs}, with appropriate minor changes in the parameters to allow for pH values not included in the results in Table 1, values of k_{corr} were obtained (Table 3).

TABLE 2

Values of kinetic parameters for the various buffers

Buffer	pH	10^5k_{corr} / s^{-1}	10^5k_a / s^{-1}	K_a / l mol^{-1}	10^5k_b / l mol^{-1} s^{-1}
Chloroacetate [a]	2·8	1·58 ±0·07			1·11 ±0·52
	3·5	1·72 ±0·06			1·38 ±0·34
Acetate [b]	4·5	1·91 ±0·02	2·27 ±0·13	7·0 ±3·0	
	5·2	2·00 ±0·05	3·08 ±0·15	4·0 ±2·0	
Monohydrogen phosphate [a]	7·1	2·58 ±0·11			13·1 ±1·2

[a] Equation (5). [b] Equation (4).

TABLE 3

Dependence of the rate constants on pH

pH	[A] / mM	10^5k_{obs} / s^{-1}	10^5k_{corr} / s^{-1}
Perchloric acid			
0·27		0·90	0·90
0·37		0·90	0·90
0·41		0·90	0·90
0·62		0·91	0·91
0·78		0·90	0·90
0·98		0·97	0·97
1·00		0·94	0·94
1·10		0·91	0·91
1·26		0·99	0·99
A = Chloroacetate			
1·58	15	1·02	1·01
1·58	15	1·03	1·02
1·65	18	1·04	1·03
1·80	24	1·06	1·05
1·88	29	1·08	1·06
2·38	69	1·38	1·32
2·55	87	1·46	1·36
2·65	100	1·62	1·51
2·72	107	1·58	1·46
2·86	123	1·74	1·60
2·91	128	1·75	1·60
3·16	152	1·90	1·69
3·32	164	1·92	1·69
A = Acetate			
3·67	21	1·83	1·80
3·72	23	1·91	1·87
3·76	25	1·84	1·80
3·80	27	2·02	1·98
3·84	29	1·77	1·72
3·85	30	1·89	1·84
4·07	45	1·89	1·82
4·27	63	1·95	1·84
4·41	77	2·01	1·89
4·50	87	1·89	1·75
4·52	90	2·02	1·88
4·55	93	1·95	1·81
4·58	97	2·03	1·89
4·58	97	2·19	2·05
4·68	108	1·97	1·82
5·22	161	2·33	1·91
5·23	161	2·32	1·90
5·26	163	2·40	1·97
5·40	172	2·40	1·95

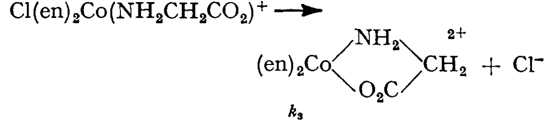
In experiments with buffers [A] + [HA] = 200mM.

It has previously been shown [5] that in a system of this kind relation (6) holds, where the constants K_1, k_2, and k_3 are

$$k_{corr} = k_3 + (k_2 - k_3)K_1/([H^+] + K_1) \quad (6)$$

defined by equations (7)—(9). From the values of k_{corr} at

$$Cl(en)_2Co(NH_2CH_2CO_2H)^{2+} \overset{K_1}{\rightleftharpoons} H^+ + Cl(en)_2Co(NH_2CH_2CO_2)^+ \quad (7)$$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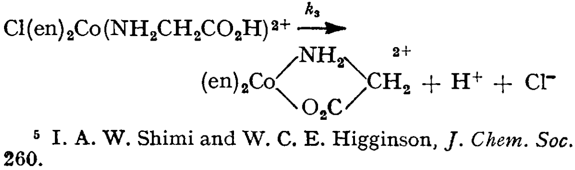
(9)

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[5] I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 1958, 260.

low pH we estimate $k_3 = (9{\cdot}00 \pm 0{\cdot}09) \times 10^{-6}\ \mathrm{s^{-1}}$. On substituting this value into equation (10), a rearranged version of (6), we obtain values of K_1 and k_2 by a weighted

$$1/(k_{\mathrm{corr}} - k_3) = 1/(k_2 - k_3) + [\mathrm{H^+}]/K_1(k_2 - k_3) \quad (10)$$

least-squares procedure, using a relative standard deviation of 3·0% for each value of k_{corr} in Table 3. In this way we find $k_2 = (1{\cdot}89 \pm 0{\cdot}02) \times 10^{-5}\ \mathrm{s^{-1}}$ and $K_1 = (3{\cdot}25 \pm 0{\cdot}26) \times 10^{-3}\ \mathrm{mol\ l^{-1}}$, corresponding to $\mathrm{p}K_1 = 2{\cdot}49 \pm 0{\cdot}04$.

The aquolead(II) cation was chosen for investigation of the effect of metal ions upon the reaction since this cation was known to be particularly effective in this type of reaction. Because of the effect of carboxylate ions upon the rate of reaction and the further complication introduced by complex formation between such anions and the lead cation, experiments at higher pH values were restricted to those conducted in pyridine buffers. Complex formation between the lead cation and pyridine appears to be small and there was little effect of pyridine buffer concentration on the rate of similar lead(II)-catalysed reactions.[2,6] The results in the presence of lead cation, summarised in Table 4, can be interpreted as follows. At pH values exceeding 4·5, less than 1% of the substrate is present in the protonated form; hence the important reactions are those of (8), (11), and (12).

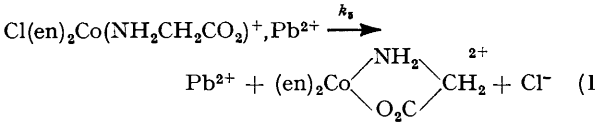
TABLE 4

Effect of lead cations upon the rate constant

pH	$[\mathrm{Pb^{II}}]$ mM	10^5k_{obs} $\mathrm{s^{-1}}$	pH	$[\mathrm{Pb^{II}}]$ mM	10^5k_{obs} $\mathrm{s^{-1}}$
0·41	100	1·28	4·98	100	17·7
0·82	100	1·70	4·64	100 *	17·3
1·32	100	3·62	4·66	125 *	18·1
4·50	100	17·3	4·68	150 *	19·4
4·80	100	17·6	4·72	175 *	20·2
4·88	100	17·4	4·75	200 *	21·2

Pyridine buffers, $r \simeq 0{\cdot}3$, $[\mathrm{Pyridine}]_{\mathrm{T}} = 0{\cdot}1\mathrm{M}$ at pH > 4.
* $[\mathrm{Pb^{II}}] + [\mathrm{Mg^{II}}] = 300\mathrm{mM}$.

$$\mathrm{Pb^{2+} + Cl(en)_2Co(NH_2CH_2CO_2)^+} \overset{K_4}{\rightleftharpoons} \mathrm{Cl(en)_2Co(NH_2CH_2CO_2)^+,Pb^{2+}} \quad (11)$$



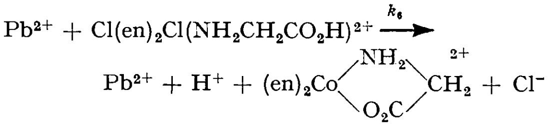
$$\mathrm{Cl(en)_2Co(NH_2CH_2CO_2)^+,Pb^{2+}} \xrightarrow{k_5} \mathrm{Pb^{2+} + \left[(en)_2Co\begin{matrix} NH_2 \\ O_2C \end{matrix}CH_2\right]^{2+} + Cl^-} \quad (12)$$

For these we obtain relation (13), where $[\mathrm{Pb^{II}}]$ represents the

$$k_{\mathrm{obs}} = k_2 + (k_5 - k_2)K_4[\mathrm{Pb^{II}}]/(1 + K_4[\mathrm{Pb^{II}}]) \quad (13)$$

total concentration of lead(II). This equation holds providing the cobalt(III) complex concentration is much smaller than $[\mathrm{Pb^{II}}]$, as is the case. Knowing k_2, we obtain, by a weighted least-squares procedure, the values $K_4 = 14{\cdot}6 \pm 4{\cdot}1\ \mathrm{l\ mol^{-1}}$ and $k_5 = (2{\cdot}75 \pm 0{\cdot}23) \times 10^{-4}\ \mathrm{s^{-1}}$ for the experiments at $0{\cdot}3\mathrm{M}$-$(\mathrm{Pb^{II}} + \mathrm{Mg^{II}})$ in Table 4. The concentration of divalent cations was kept constant in this group of experiments so that the ionic strength could be maintained at 1·00M without changing the perchlorate-ion concentration within the group, which would occur if sodium perchlorate were used to replace lead perchlorate. In fact, comparison between these results and those at pH 4—5 in the absence of magnesium perchlorate shows that the anticipated effect is negligible.

In the experiments at pH 0·4—1·3, the bulk of the cobalt substrate is in its protonated form and reactions (7), (9), and (14) must also be taken into account.



$$\mathrm{Pb^{2+} + Cl(en)_2Cl(NH_2CH_2CO_2H)^{2+}} \xrightarrow{k_6} \mathrm{Pb^{2+} + H^+ + \left[(en)_2Co\begin{matrix} NH_2 \\ O_2C \end{matrix}CH_2\right]^{2+} + Cl^-} \quad (14)$$

Since the association (11) between $\mathrm{Pb^{2+}}$ and the glycinato-*N* complex presumably involves the free carboxylate group of the latter, there is no need to introduce a similar association equilibrium between $\mathrm{Pb^{2+}}$ and the glycine-*N* complex, because the carboxylate group of the latter is protonated. We may now write equation (15), where the four terms on the right-hand side

$$k_{\mathrm{obs}}([\mathrm{H^+}]/K_1 + K_4[\mathrm{Pb^{II}}] + 1) = k_3[\mathrm{H^+}]/K_1 + k_6[\mathrm{H^+}][\mathrm{Pb^{II}}]/K_1 + k_2 + K_4k_5[\mathrm{Pb^{II}}] \quad (15)$$

are related to reaction paths involving $\mathrm{Cl(en)_2Co(NH_2CH_2CO_2H)^{2+}}$, $\mathrm{Cl(en)_2Co(NH_2CH_2CO_2H)^{2+} + Pb^{2+}}$, $\mathrm{Cl(en)_2Co(NH_2CH_2CO_2)^+}$, and $\mathrm{Cl(en)_2Co(NH_2CH_2CO_2)^+ + Pb^{2+}}$ respectively. Equation (15) can be rearranged to give (16). We can calculate k_{obs} using (16) if we omit the term in

$$k_{\mathrm{obs}} = k_3 + k_6[\mathrm{Pb^{II}}]/Q + (k_2 - k_3)K_1/Q[\mathrm{H^+}] + K_1K_4(k_5 - k_3)[\mathrm{Pb^{II}}]/Q[\mathrm{H^+}] \quad (16)$$

with $$Q = 1 + K_1K_4[\mathrm{Pb^{II}}]/[\mathrm{H^+}] + K_1/[\mathrm{H^+}]$$

k_6, since the other constants are already known. With this omission, we calculate 10^5k_{obs} to be 1·30, 1·89, and 3·73 $\mathrm{s^{-1}}$ for the experiments at pH 0·41, 0·82, and 1·32, respectively. Since the calculated values are slightly higher than those observed, it is evident that, under these conditions, the term in k_6 is unimportant.

DISCUSSION

In this chelation reaction, the parent complex *cis*-chlorobis(ethylenediamine)glycinato-*N*-cobalt(III) has been found to react twice as rapidly as its conjugated acid, in which the free carboxylate group is protonated. In the similar reaction of chloro(ethylenediaminetriacetatoacetate)cobaltate(III), the substrate reacts only one third faster than the corresponding protonated form.[1] The effect in the latter case seemed too small to permit mechanistic conclusions to be reached; because of the different charges of the substrate and its protonated form, the difference in reactivity might be a salt effect. However, the similar but larger ratio of reactivity with the glycinato-*N* complex and its conjugate acid, complexes of opposite charge to the edta complexes, now leads us to suggest that in the reactions of both the basic forms there is weak bond-making by the incoming carboxylate group. [We prefer this interpretation to one based on intermediate formation of an aquo-complex; the high reactivity of the latter in the edta system, and the lack of evidence for an aquo-complex corresponding to $\mathrm{Cl(en)_2Co(NH_2CH_2CO_2)^+}$ precludes a simple experimental distinction.] These reactions belong only marginally to the (internal) $S_{\mathrm{N}}2$ type, owing to repulsion between the similarly charged leaving chloride ion and

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[6] W. C. E. Higginson and M. P. Hill, *J. Chem. Soc.*, 1959, 1620.

the entering carboxylate group. When such repulsion is reduced, as in metal-ion catalysis of these reactions, or in loss of the water ligand from (ethylenediaminetriacetatoacetate)aquocobaltate(III),[5] much larger reactivity ratios are found between the substrate and its conjugate acid.

In the Pb^{2+}-assisted loss of chloride ion from chloro(ethylenediaminetriacetatoacetate)cobaltate(III), the rate of reaction is *ca.* 240 times that of the conjugate acid,[2] while the corresponding ratio in the Pb^{2+}-assisted reactions of the glycinato-*N* and glycine-*N* complexes exceeds 200. We note that there is evidence of association between Pb^{2+} and the base form of the substrate in both of these reactions, the association constant for the glycinato-*N* complex, $K_4 = 15$ l mol^{-1}, being similar to that for the edta complex, 23 l mol^{-1},[1] even though the charges on these two substrates are of opposite sign. This is evidence that the association is primarily with the free carboxylate group. The high value of the ratio referred to above is evidence that interaction between Pb^{2+} and the chloride ligand alone does not lead to a major reaction path.

Our value of $pK_1 = 2{\cdot}5$ is not in very good agreement with that, 2·1, quoted by Alexander and Busch, but the experimental conditions differ markedly in the two cases. In the analysis of the dependence of k_{obs} on pH which led to our value of pK_1 we excluded the high value of k_{corr} obtained at pH 7·1, *ca.* 30% higher than the corresponding values obtained at pH 5, even though the substrate is almost entirely in its base form at the latter pH. This value may indicate the occurrence of a path involving the conjugate base of the substrate $Cl(en)_2Co(NH_2CH_2CO_2)^+$.

The effects of buffer concentration on the rate constant, summarised in Table 1, appear to be caused by the buffer base, since this implies a similar effect of a given base concentration at different pH values. Were the increase in rate ascribed to the buffer acid, it would be necessary to explain its considerably greater effectiveness in solutions of higher pH. Although the curvature of the plots of k_{obs} against acetate concentration, particularly at pH 5·1, may indicate a substantial degree of association between this buffer base and the substrate, such curvature was not observed with chloroacetate or hydrogenphosphate buffers. Since the standard deviations of the association constants deduced for acetate are large, we do not attach any special importance to the apparently large association with this anion. The effects of these anions are relatively small and, since the substrate is positively charged, it is possible that these are due to salt effects. However, the effectiveness of these anions, as measured by values of k_b, that for acetate being *ca.* $3{\cdot}4 \times 10^{-5}$ l mol^{-1} s^{-1}, shows an increase with increasing base strength of the anion. This may indicate a specific chemical effect, such as participation by the buffer in a conjugate base type of mechanism.

EXPERIMENTAL

cis-Chlorobis(ethylenediamine)glycine-*N*-cobalt(III) dichloride was prepared *via* its methyl ester as previously described.[4] Microanalysis for C, H, N, and Cl and comparison of the visible spectrum in aqueous solution with that previously obtained [4] were consistent with the presence of 1·0 mole of water per mole of complex in our material. This acid form of the complex was used in making up all solutions for kinetic experiments, irrespective of pH, the final concentration of the complex plus its conjugate base being *ca.* 6mM. The initial product and a recrystallised sample gave identical kinetic results. Sodium perchlorate was B.D.H. ' low in chloride ' quality; other reagents were of B.D.H. AnalaR grade.

Lead perchlorate solutions were obtained by dissolving lead carbonate in a small excess of perchloric acid (60%) followed by boiling, filtering, and diluting to 2M; the lead carbonate was prepared by double decomposition between lead nitrate and sodium carbonate. Magnesium perchlorate solutions were obtained by dissolving magnesium oxide in perchloric acid (60%), filtering, and diluting to 2M. The divalent cation concentration in these solutions was determined by titration against a standard edta (disodium dihydrogen salt) solution. The total equivalent concentration of cations in these and sodium perchlorate stock solutions was estimated by passing aliquot portions down a column of Amberlite IR-120H resin, followed by titration against standard sodium hydroxide solution. Other stock solutions were standardised by conventional methods.

A Unicam SP 600 spectrophotometer was employed for measuring the optical density at 550 nm of samples of the reaction mixtures, taken at appropriate intervals of time during kinetic experiments. The spectrum of the glycine-*N* complex was obtained by using a Hilger Uvispek spectrophotometer. All pH measurements on reaction mixtures were made at 20 °C; the temperature difference between these measurements and kinetic experiments at 45·0 ± 0·1 °C is probably partly responsible for the discrepancy between our value of pK_1 and that previously obtained. The pH meter was standardised with a 0·05M-potassium hydrogen phthalate solution. Because of the high concentration of perchlorate ions in reaction solutions, it was necessary to use saturated sodium chloride solution in the calomel electrode.

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