# VOLTAMMETRIC STUDY OF CHLORINE USING A ROTATING GOLD DISC ELECTRODE

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The kinetics of hydrolysis of chlorine in acidic aqueous solutions was studied by the voltammetric method using a rotating gold disc electrode. The voltammetric curves consist of two waves, of which the more negative corresponds to reduction of hypochlorous acid and the more positive to reduction of chlorine. The wave of chlorine increases with the concentration of $H^+$ and $Cl^-$ ions and has a kinetic character; in acetate buffer (pH 3·6) its behaviour approaches best the theory of kinetic-controlled waves. The corresponding dependences on the concentrations of $H^+$ and $Cl^-$ ions, however, show some anomalies suggesting complications in the reaction mechanism.

In the field of chlorine chemistry, which has a considerable practical importance especially in water treatment and industrial sewage processing, many works have been published dealing both with the determination of chlorine in various oxidation states and with their equilibria. Voltammetry with a rotating disc electrode has been used to elucidate some catalytic phenomena due mainly to iridium and rhodium admixtures in platinum electrodes used in studies of the reduction of chlorine or oxidation of chlorides[1−5]. Although the literature in the field of voltammetry of chlorine is very voluminous, the kinetic behaviour of chlorine and $ClO^-$ ions on a rotating disc electrode has hitherto not been described. This phenomenon is dealt with in the present work.

## EXPERIMENTAL

### Reagents

All chemicals used were of reagent grade. Constant ionic strength 0·4 was maintained by adding a weighed quantity of $Na_2SO_4$. Before voltammetric measurements, the solutions were deaerated with nitrogen purified with an alkaline solution of sodium anthraquinonesulphonate and an acidic solution of Cr(II) ions. Stock solution of chlorine was prepared by bubbling chlorine through redistilled water for half an hour; the resulting concentration was about 0·05 mol l$^{-1}$. The solution was stored in the dark at 5—10°C and was freshly prepared every week. The con-

centration of $Cl_2$ was determined iodometrically: a solution of KI was added to a sample solution acidified with $H_2SO_4$ and the iodine set free was titrated with thiosulphate. The content of chlorine in the electrolysed solutions was determined both before recording voltammetric curves in a separate sample solution and after recording in the solution used. When a series of curves was recorded with the use of the same solution, the content of $Cl_2$ between successive recordings was estimated by interpolation.

### Apparatus

A rotating gold disc electrode was prepared according to Beran and Opekar[6] from a hollow Teflon cylinder into which a brass piece with a gold disc was pressed at elevated temperature (200°C). The surface of the disc was ground with abrasive papers and polished with metallographic $Al_2O_3$ powder (Chemiewerk Greiz-Dolau, G.D.R.). The electrode was polarized before the measurements in $0.1M$-$HClO_4$ from $+0.4$ to $-1.3$ V at a low rotation speed. In the course of work, it was polished from time to time with velvet and washed with saponate, dilute $H_2SO_4$ and distilled water. Unless otherwise indicated, the rotation speed was 440 rpm.

The electrolytic vessel of 250 ml holding capacity was provided with a thermostated mantle piece and contained the rotating disc electrode, a reference calomel electrode (Radiometer K 401) with a salt bridge, an auxiliary gold electrode separated with a glass frit, and a tube for bubbling nitrogen.

Voltammetric curves were recorded on a PA 3 polarograph with an XY 4105 recorder (Laboratorní přístroje, Prague); the sweep rate was $10-20$ mV/s. The temperature was kept at 20°C by a U 3 thermostat (Prüfgeräte-Werk Medingen, G.D.R.). Titrations were performed on a Radiometer titration set-up including TTT 60 titrator, Rec 61 Servograph, PHM 64 pH meter, TTA 3 device and ABU 12 autoburette (burette volume 2.5 ml, accuracy $\pm 0.001$ ml). Values of pH were measured by a pH meter Radiometer PHM 83 with a glass electrode G 202 C.

### THEORETICAL

#### Hydrolytic Equilibrium

The following hydrolytic equilibrium is established in aqueous solutions of chlorine

$$Cl_2 + H_2O \quad \underset{k_r}{\overset{k_h}{\rightleftharpoons}} \quad HOCl + H^+ + Cl^- \qquad (A)$$
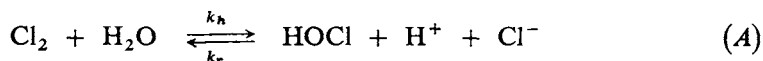
together with dissociation of hypochlorous acid.

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (B)$$

We shall assume that the concentration of hydrogen ions is known (i.e. that the solution is buffered) and that the concentration of water is constant (i.e. in large excess). We introduce the notation

$$[Cl_2] = c_1, \quad [HOCl] = c_2, \quad [H_3O^+] = c_3, \quad [Cl^-] = c_4, \quad [OCl^-] = c_5.$$

The unknown concentrations can be found from the following equations or definitions:

The hydrolysis constant

$$K_h = c_2 c_3 c_4 / c_1 , \qquad (1)$$

the dissociation constant

$$K_a = c_3 c_5 / c_2 , \qquad (2)$$

analytical concentration of chlorine

$$c_a = c_1 + c_2 + c_5 , \qquad (3)$$

and concentration of hypochlorite

$$c_2 + c_5 = c_4 . \qquad (4)$$

To be more general, let us assume that chloride ions in a concentration $c_{4a}$ were present in the solution already before adding chlorine. Then, Eq. (4) will be replaced by

$$c_2 + c_5 = c_4 - c_{4a} . \qquad (4a)$$

If we introduce the quantity $p$ defined as

$$p = K_h / c_3 c_a + c_3 c_{4a} / c_a (K_a + c_3)$$

then the solution of Eqs (1)−(4a) can be written in the form

$$c_2 / c_a = -p/2 + [p^2/4 + K_h / c_a (K_a + c_3)]^{1/2} \qquad (5)$$

$$c_1 / c_a = 1 - c_2 / c_a - c_5 / c_a , \qquad (6)$$

$$c_4 / c_a = 1 + c_{4a} / c_a - c_1 / c_a , \quad c_5 / c_a = K_a c_2 / c_3 c_a . \qquad (7), (8)$$

The values of the constants can be taken from Snoeyink and Jenkins[7]:

$$K_h = 4 . 10^{-4} \, mol^2 \, l^{-2} , \quad K_a = 10^{-7.5} \, mol \, l^{-1} .$$

Similar values of $K_h$ were published by Jakowkin[8] ($3.9 . 10^{-4}$), Shilov[9] ($4.75 . 10^{-4}$), and Zimmermann[10] (($3.35 \pm 0.11) . 10^{-4}$). The mean of all four values is $4.0 . 10^{-4} \, mol^2 \, l^{-2}$.

*Kinetic Current on the Rotating Disc Electrode*

We shall assume the following pseudomonomolecular reaction scheme:

$$HCl + HOCl \underset{\sigma\varrho}{\overset{\varrho}{\rightleftharpoons}} Cl_2 + H_2O, \quad Cl_2 + 2e^- \rightarrow 2Cl^-, \quad (C)$$
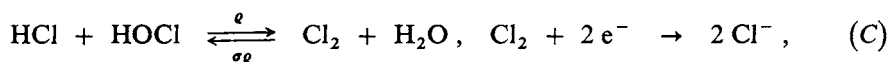
where the equilibrium is shifted to the left-hand side $(\sigma \gg 1)$. The concentrations of chloride and hydrogen ions change during the reaction, but we shall assume that the changes are negligible. A comparison with the equilibrium $(A)$ reveals that

$$\varrho\sigma = k_h, \quad \varrho = k_r[H^+][Cl^-], \quad (9)$$

$$\sigma = k_h/k_r[H^+][Cl^-] = K_h/[H^+][Cl^-]. \quad (10)$$

The kinetic current corresponding to the reaction scheme $(C)$ is given by the equation[6,11]

$$i_k = i_d \left[1 + \frac{\sigma}{1\cdot61}\left(\frac{\omega}{\varrho(1+\sigma)}\right)^{1/2}\left(\frac{D}{v}\right)^{1/6}\right]^{-1} \quad (11)$$

which on neglecting 1 against $\sigma$ and substituting the expressions $(9)$ and $(10)$ for $\varrho$ and $\sigma$ can be rearranged in the form

$$\frac{i_k}{i_d - i_k} = \frac{1\cdot61}{\sqrt{\omega}}\left(\frac{v}{D}\right)^{1/6}\left(\frac{k_r}{K_h}\right)^{1/2}[H^+][Cl^-]. \quad (12)$$

This equation is preferable since it leads to a linear concentration dependence and it does not require exact knowledge of the concentration of chlorine.

Now, it is necessary to have a value of the diffusion coefficient $D$ of chlorine in water. It can be calculated from the approximate equation

$$D = kT/6\pi\eta r, \quad (13)$$

where $k$ is Boltzmann's constant, $\eta$ is viscosity of the solution, and $r = 0\cdot185$ nm is the radius of the $Cl_2$ molecule[12]. For $\eta = 1\cdot0 . 10^{-3}$ kg m$^{-1}$ s$^{-1}$ we obtain $D = 1\cdot16 . 10^{-9}$ m$^2$ s$^{-1}$ (20°C), $v = 1\cdot0 . 10^{-6}$ m$^2$ s$^{-1}$, and $D/v = 1\cdot16 . 10^{-3}$. A necessary condition for the validity of the solution $(12)$ is, besides $\sigma \gg 1$, also[6]

$$\left(\frac{\omega}{\varrho(1+\sigma)}\right)^{3/2}\sqrt{\frac{D}{v}} \ll 1, \quad (14)$$

where $\varrho(1 + \sigma) \approx \varrho\sigma = k_r K_h = k_h$. In our case, the fulfillment of the condition (14) requires that the rotation speed be as low as possible. For this reason, we practically could not use the dependence of $i_k/\sqrt{\omega}$ on $i_k$ recommended by Vielstich[11].

## RESULTS AND DISCUSSION

The dependences of the kinetic current $i_k$ and total (diffusion) current $i_d$ of both waves on the concentrations of $Cl^-$ and $H^+$ ions at 440 rpm ($\omega = 46.08 \text{ s}^{-1}$) showed that at low pH values (from 1 to 2·2) and low concentrations of added chloride (up to 0·006 mol $l^{-1}$) the prewave is well developed (Fig. 1), however the condition (14), requiring $k_r \gg 1·2 \cdot 10^4 \, l^2 \, mol^{-2} \, s^{-1}$, is not satisfied; and the condition $\sigma \gg 1$ is not satisfied in some cases.

The dependence on the concentration of added NaCl led to the results summarized in Table I. The values of $[Cl^-]$ in Eq. (12) were calculated from the hydrolytic equilibrium of chlorine and the added NaCl according to Eqs (5)–(8). The tabulated data refer to cases where the dependence of $i_k/(i_d - i_k)$ on $[Cl]^-$ was practically linear (Fig. 2) (for records Nos 1 and 7 it passed through the origin of coordinates, whereas for others the section on the axis of ordinates was 0·05–0·11).

The dependence of $i_k/(i_d - i_k)$ on $[H^+]$ is analogous and the results are summarized in Table II. The straight line passed through the origin of coordinates in all cases.

The calculated values of $k_r$ show a considerable scatter; the mean value of all measurements (Tables I and II) is $(8·2 \pm 3·1) \cdot 10^3 \, l^2 \, mol^{-2} \, s^{-1}$. It is apparent that the deviation from the mean is largest for those cases where the parameter $\sigma$ was minimal (Nos 7 and 8 in Table I), thus violating the condition $\sigma \gg 1$. If we omit these cases, the mean value of $k_r$ is $(7·1 \pm 1·8) \cdot 10^3 \, l^2 \, mol^{-2} \, s^{-1}$. For the reasons given above, even this value must be considered as rough, perhaps as a phenomenological value.

The situation looks better at higher pH values in an acetate buffer. The assumptions for the validity of the theory are here satisfied. The dependence on the concentration of $Cl^-$ ions at pH 3·6 (Fig. 3) leads to the results summarized in Table III. The dependence of $i_k/(i_d - i_k)$ on the concentration of $Cl^-$ ions is approximately linear; the section on the axis of ordinates is equal to 0·014–0·018, corresponding to the first three lines in Table III. A larger deviation from linearity was observed for the record No. 4 in Table III; from this the Fig. 4 was obtained. For the record No. 5, the section on the axis of ordinates was 0·04. The kinetic waves of chlorine were lowest for the record No. 1, since the chloride concentration was low; this caused some errors in measuring the wave heights, which however are not entirely responsible for the high value of $k_r$. With decreasing concentration of $Cl^-$ ions, the slope of the concentration dependence and hence the value of $k_r$ calculated from it tends to increase in all cases.

TABLE I

Values of $\sigma$ and $k_r$ calculated from the dependence of $i_k$ on [NaCl] in solutions of $H_2SO_4$, $Na_2SO_4$ and NaCl ($\mu = 0.4$); concentration of chlorine $3-5 \cdot 10^{-4}$ mol $l^{-1}$

| No. | $[H^+]$ mol $l^{-1}$ | [NaCl] mol $l^{-1}$ | $k_r \cdot 10^{-3}$ $l^2$ mol$^{-2}$ s$^{-1}$ | $\sigma$ |
|-----|------|------|------|------|
| 1 | 0.03 | 0—0.005 | 6.9 | 2.5—38.7 |
| 2 | 0.03 | 0—0.006 | 5.3 | 2.1—34.8 |
| 3 | 0.03 | 0—0.006 | 7.0 | 2.1—33.4 |
| 4 | 0.03 | 0—0.005 | 6.8 | 2.5—10.1 |
| 5 | 0.06 | 0—0.0024 | 6.0 | 2.5—21.2 |
| 6 | 0.06 | 0—0.0028 | 9.7 | 2.2—21.2 |
| 7 | 0.10 | 0—0.005 | 12 | 0.78—10.7 |
| 8 | 0.10 | 0—0.002 | 15 | 1.7—8.5 |



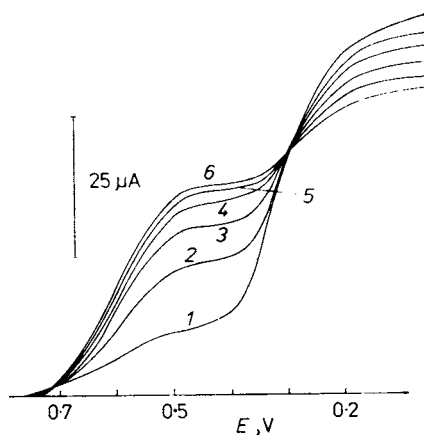FIG. 1

Voltammetric curves for chlorine at various concentrations of chloride ions. Electrolyte 0.05M-$H_2SO_4$ and 0.083M-$Na_2SO_4$ ($\mu = 0.4$), rate of potential scan 20 mV s$^{-1}$. Concentration of Cl$^-$ in mmol dm$^{-3}$: 1 0.374 (0); 2 1.293 (1.0); 3 2.239 (2.0); 4 3.199 (3.0); 5 4.167 (4.0); 6 5.144 (5.0) (values in parentheses refer to additions of Cl$^-$ ions); concentration of Cl$_2$ before and after the experiment: 0.409 and 0.329 mmol dm$^{-3}$
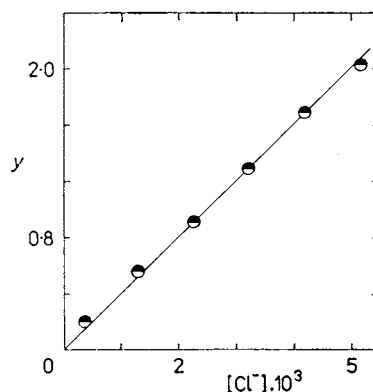


FIG. 2

Dependence of $y = i_k/(i_d - i_k)$ on the concentration of Cl$^-$ ions according to Fig. 1

The dependence on the concentration of hydrogen ions in acetate buffer (pH $3\cdot6-4\cdot6$) gives the results in Table IV. For $[H^+] < 10^{-4}$ mol $l^{-1}$ the dependence of $i_k/(i_d - i_k)$ on $[H^+]$ from the records Nos 1 and 2 (Table IV) deviates from

TABLE II

Values of $\sigma$ and $k_r$ calculated from the dependence of $i_k$ on pH in solutions of $H_2SO_4$, $Na_2SO_4$, and NaCl ($\mu = 0\cdot4$); concentration of chlorine $2-3 \cdot 10^{-4}$ mol $l^{-1}$

| No. | $[H^+]$ mol $l^{-1}$ | $[NaCl]$ mol $l^{-1}$ | $k_r \cdot 10^{-3}$ $l^2$ mol$^{-2}$ s$^{-1}$ | $\sigma$ |
|---|---|---|---|---|
| 1 | $0\cdot010-0\cdot060$ | $0\cdot002$ | $4\cdot9$ | $3\cdot0-17\cdot3$ |
| 2 | $0\cdot006-0\cdot056$ | $0\cdot003$ | $6\cdot7$ | $2\cdot2-20\cdot2$ |
| 3 | $0\cdot006-0\cdot086$ | $0\cdot003$ | $10\cdot8$ | $1\cdot5-20\cdot4$ |
| 4 | $0\cdot006-0\cdot106$ | $0\cdot003$ | $7\cdot0$ | $1\cdot2-20\cdot4$ |

TABLE III

Values of $\sigma$ and $k_r$ calculated from the dependence of $i_k$ on [NaCl] in acetate buffer at pH $3\cdot6$

| No. | $[NaCl]$ mol $l^{-1}$ | $k_r \cdot 10^{-4}$ $l^2$ mol$^{-2}$ s$^{-1}$ | $[Cl_2] \cdot 10^4$ mol $l^{-1}$ | $\sigma$ |
|---|---|---|---|---|
| 1 | $0-0\cdot025$ | $14\cdot5$ | $6\cdot0-6\cdot64$ | $62-2\,437$ |
| 2 | $0-0\cdot076$ | $6\cdot1$ | $2\cdot7-3\cdot2$ | $20\cdot7-1\,702$ |
| 3 | $0-0\cdot08$ | $5\cdot4$ | $8\cdot61-9\cdot36$ | $19\cdot8-2\,419$ |
| 4 | $0\cdot008-0\cdot1$ | $5\cdot4$ | $6\cdot10-7\cdot10$ | $15\cdot9-191$ |
| 5 | $0\cdot02-0\cdot14$ | $5\cdot3$ | $6\cdot02-6\cdot64$ | $11\cdot3-76\cdot9$ |

TABLE IV

Values of $\sigma$ and $k_r$ calculated from the dependence of $i_k$ on pH in acetate buffer at pH $3\cdot6-4\cdot6$

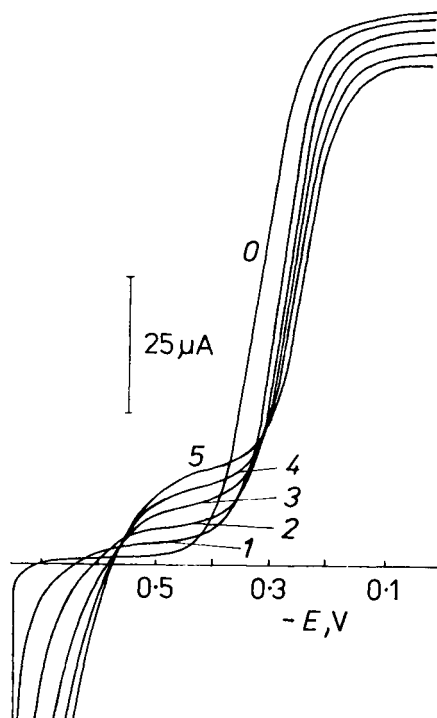| No. | $[NaCl]$ mol $l^{-1}$ | $k_r \cdot 10^{-4}$ $l^2$ mol$^{-2}$ s$^{-1}$ | $[Cl_2] \cdot 10^4$ mol $l^{-1}$ | $\sigma$ |
|---|---|---|---|---|
| 1 | $0\cdot16$ | $1\cdot05$ | $7\cdot6 \ -9\cdot1$ | $9\cdot9-94\cdot6$ |
| 2 | $0\cdot20$ | $1\cdot9$ | $8\cdot15-8\cdot6$ | $8\cdot1-79\cdot3$ |
| 3 | $0\cdot20$ | $2\cdot0$ | $7\cdot15-7\cdot46$ | $7\cdot9-79\cdot4$ |

FIG. 3

Voltammetric curves for chlorine in acetate buffer (pH 3·6) at various concentrations of $Cl^-$ ions. Rate of potential scan 20 mV $s^{-1}$. Concentration of $Cl^-$ in mmol dm$^{-3}$: 0 0·66 (0); 1 8·64 (8·0); 2 20·6 (20·0); 3 40·6 (40); 4 60·6 (60); 5 85·8 (85) (values in parentheses refer to additions of $Cl^-$ ions); concentration of $Cl_2$ before and after the experiment: 0·66 and 0·60 mmol dm$^{-3}$
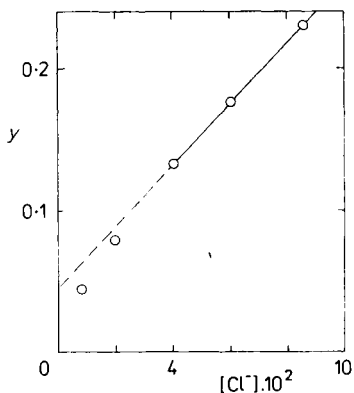


FIG. 4

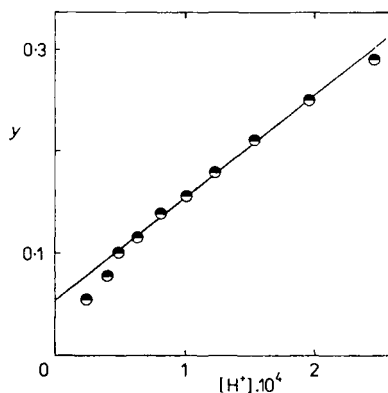Dependence of $y = i_k/(i_d - i_k)$ on the concentration of $Cl^-$ ions according to Fig. 3



FIG. 5

Dependence of $y = i_k/(i_d - i_k)$ on the concentration of hydrogen ions in acetate buffer at $[Cl^-] = 0·2$ mol dm$^{-3}$ and $[Cl_2] = 8·2 \cdot 10^{-4}$ mol dm$^{-3}$

a straight line (Fig. 5). The condition (14) is not satisfied and it seems that the dependence on pH is more complicated than would correspond to the reaction scheme considered; possibly the general acid-base catalysis comes into play.

For the sake of comparison, we also plotted the dependences of $i_k/\sqrt{\omega}$ on $i_k$ according to Vielstich[11], whose slope was negative as expected and suggested that the prewave of chlorine is kinetic in nature. The evaluation of these diagrams was, however, problematical since they were nonlinear and convex with respect to the current axis. The kinetic character of the chlorine prewave is further supported by the fact that its height was in all cases larger than would correspond to the equilibrium concentration of chlorine in solution. This increase of the wave height was most pronounced in the medium of acetate buffer (up to a factor of 4 as in Fig. 3). Nevertheless, our observations suggest that the prewave of chlorine is not "purely" kinetic, i.e. that the equilibrium concentration of chlorine is mostly not negligible and the chemical reaction of its formation is not sufficiently rapid.

It would thus seem that the theory[13] derived for kinetic currents with arbitrarily rapid preceding chemical reaction is more suitable for our case. However, calculations carried out by us showed that the more general theory does not fit better the experimental data: the measured dependences of the kinetic wave on the concentrations of $Cl^-$ and $H^+$ ions again deviated from the calculated course.

The dependences of the kinetic current $i_k$ of chlorine and of the diffusion current $i_d$ of hypochlorous acid on the temperature are given in Table V, where the approximate values of $\sigma$ are also indicated. The condition of the kinetic current is satisfied for the records Nos 3 and 4 ($\sigma \gg 1$). The temperature coefficients were determined from the plot of the current against temperature, which was approximately linear (except for the record No. 2), and are only approximate. Nevertheless, it can be said that the temperature dependences of both waves are roughly the same. The dependence of the diffusion current of HClO on the temperature is in substance given by the dependence of the diffusion coefficient or $D^{2/3}$ on the temperature, which is

TABLE V
Dependence of the kinetic current of chlorine, $i_k$, and of the total diffusion current, $i_d$, on the temperature at 5—25°C

| No. | pH | [NaCl] mol $l^{-1}$ | $d\ln i_k/dT$ | $d\ln i_d/dT$ | $\sigma$ |
|---|---|---|---|---|---|
| 1 | 1·52 | 0·002 | 0·029 | 0·029 | 5·8 |
| 2 | 1·52 | 0·004 | 0·023 | 0·029 | 3·1 |
| 3 | 3·60 | 0·20 | 0·034 | 0·025 | 80 |
| 4 | 3·60 | 0·20 | 0·017 | 0·017 | 80 |

normally $1-2\%$ per degree. The dependence of $i_k$ on $T$ follows from Eq. $(11)$ or $(12)$, hence it is given by the dependence of the term $\sqrt{(k_r/K_h)}$ on $T$. This may be rather small, since some compensation of the dependences of $k_r$ and $K_h$ takes place. For this reason, the temperature coefficient of the kinetic wave need not necessarily be much higher than that of the diffusion wave.

Since the hydrolysis constant $K_h$ is equal to the ratio of the rate constants of hydrolysis and recombination, $k_h/k_r$, it depends on $T$ less than the rate constants, hence the ratio of $k_r/K_h$ should increase with the temperature. In our case, however, this does not seem to be the case, since the ratio of $i_k/(i_d - i_k)$ in Eq. $(12)$ is practically independent of the temperature.

The rate constant $k_r$ is difficult to interpret physically, since a trimolecular reaction appears rather improbable. For this reason, our kinetic data must be considered as phenomenological in character: their discussion would require knowledge of the mechanism of the reaction of hypochlorous acid with chloride ions in acidic medium.

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