ionized carboxylic acids,[17] giving strong bands in the regions 1610–1550 cm.$^{-1}$ (symmetrical vibrations) and 1420–1300 cm.$^{-1}$ (asymmetrical).

On the anatase, the $CO_2^-$ species is predominant as the two strong bands at 1580 and 1320 cm.$^{-1}$ fall well within the usual range for such species. The 1580 cm.$^{-1}$ band is stronger than the 1320 cm.$^{-1}$ band, however. The weak shoulder at about 1500 cm.$^{-1}$ is more difficult to assign; it does not fall into either the $CO_2^-$ or $CO_3^-$ region, but is only just outside the region normally assigned to carbonates (1450–1410 cm.$^{-1}$). It is tentatively suggested that this shoulder is caused by a small proportion of carbonate-like species on the surface.

**Rutile.**—The width of the bands (Fig. 4) is very similar to that found with anatase, and the significance of this has been discussed in the previous section. The strong band at 1325 cm.$^{-1}$ and the weak shoulder at 1580 cm.$^{-1}$ may be due to some type of $CO_2^-$ species. However, if sufficient of these species are present to form a strong band due to asymmetric stretching vibrations at 1325 cm.$^{-1}$, it is difficult to account for the weakness of the band at 1580 cm.$^{-1}$, presumably due to the symmetrical stretching vibrations. It seems very unlikely that the extinction coefficients of these two modes of vibration of the $CO_2^-$ species could be drastically affected by the surface on which they are adsorbed. The assignment of the bands on the rutile surface is rather uncertain for this reason. The strong band at 1485 cm.$^{-1}$ shown in Fig. 4a may be caused by a carbonate-like species. Although outside the range normally assigned to carbonates (1450–1410 cm.$^{-1}$) this may be because these surface species do not have any strictly comparable analogs in bulk solids. Possibly configurations intermediate between a carboxylate and a carbonate group are present on the surface.

More work is needed before such species, if they exist, can be assigned with certainty. What is certain is that carbon dioxide is strongly adsorbed on the samples of anatase and rutile used here, probably both as $CO_2^-$ and $CO_3$ species. Nevertheless, wide variations in intensity of the 1580 and 1485 cm.$^{-1}$ bands occur when anatase and rutile are compared.

In common with the spectra of the residual hydroxyl groups and carbon monoxide, the spectra of the chemisorbed carbon dioxide show clearly that there are quite wide differences in surface properties between the two samples. While this may be due to the different bulk crystal structure of the two oxides, this is unlikely, as very large differences in the spectra of the residual OH groups were found between the anatase and rutile mainly used, and the other samples also studied. The marked differences in surface characteristics shown in all the figures for anatase (MP-1579) and rutile (MP-1208) are likely to be due to variations in their method of manufacture. With titania, at least, it is evident that a great deal of care must be taken in sample selection before the experimental data obtained can bear any relation to surface properties which may be calculated from bulk values of lattice constants, crystal structure, polarizability and so on.

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# THE KINETICS OF THE HYDROLYSIS OF CHLORINE. II. THE HYDROLYSIS IN THE PRESENCE OF ACETATE

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The hydrolysis of chlorine in the presence of acetate ions has been investigated. The results can be explained by the assumption that the reaction proceeds along three parallel paths: one the same as in pure water, the second involving a reaction between molecular chlorine and acetate ions, and the third involving a reaction between molecular chlorine and hydroxyl ions. In the presence of acetate and acetic acid the second reaction predominates and its rate constant can be determined ($k = 5.5_5 \times 10^2$ mole$^{-1}$ l. sec.$^{-1}$). In the presence of acetate alone, the second and third reactions make comparable contributions. The rate constant for the third reaction can only be estimated approximately. In order to contribute to the observed rate, this reaction must be diffusion-controlled.

## Introduction

We have reinvestigated recently[1] the kinetics of the hydrolysis of chlorine in pure water, using the continuous flow method. We concluded that the reaction takes place according to

$$X_2 + H_2O \rightleftarrows HOX + X^- + H^+ \qquad (1)$$

(where X represents the halogen) with no appreciable contribution from a reaction involving the hydroxyl ion

$$X_2 + OH^- \rightleftarrows HOX + X^- \qquad (2)$$

On the other hand, when investigating the kinetics of the hydrolysis of bromine[2] in phosphate buffer solution we found that the observed rate was compatible with the mechanism

$$H_2O + X_2 + A^- \rightleftarrows HOX + X^- + HA \quad (3)$$

where $A^-$ represents the buffer anion. The next step in our program of investigating the kinetics of the hydrolysis of the halogens is the study of the hydrolysis of chlorine in buffer solution in order to verify whether mechanism 3 is operative for chlorine. In this paper, the results in the presence of acetate are reported; the possible correla-

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[1] A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, **64**, 1663 (1960).

[2] A. Lifshitz and B. Perlmutter-Hayman, *Bull. Research Council Israel*, **A8**, 166 (1959).

tion between $k_{A^-}$ and the basic strength of $A^-$ will be discussed in a later paper.

## Experimental

We again used the continuous flow method, where the progress of the reaction along the observation tube was measured with the aid of 8 thermistors. The apparatus and experimental procedure are described elsewhere.[1,3] The flow velocity was 4.5 to 7.7 cc. sec.$^{-1}$ (140 to 250 cm. sec.$^{-1}$). Chlorine water was prepared and analyzed as before.[1] When the hydrolysis in the presence of acetate only was investigated, the latter was contained in one vessel, and the chlorine solution in the other. Other reagents (acetic acid or inert salt) were divided to equal parts between the two reactant vessels. The concentration of the acetate was checked by adding to a sample a known amount of standard HCl solution, and carrying out a conductometric titration of the excess HCl, using standard NaOH solution. The temperature was again[1] 9.5°. The total temperature change $\Delta T_\infty$ was between ($-141$ to $-296$) $\times 10^{-3}$ deg.

## Results

**Influence of Ionic Strength.**—An experiment was carried out in the presence of 0.17 $N$ sodium perchlorate. Within the limit of experimental error the rate constant $k_{H_2O}$ ($k_1$ of our previous paper) was identical with that found previously for the reaction in pure water.

**Experiments in the Presence of Sodium Acetate, and of Sodium Acetate and Acetic Acid.**—Experiments at various initial concentrations of chlorine, sodium acetate and acetic acid were carried out. Details of these experiments are summarized in Table I. In this table, $a$ is the total stoichiometric concentration of chlorine and $x_0$ and $x_e$ are the concentrations of chloride (or hypochlorous acid) at time zero and infinity, respectively. The values of $x_0$ were calculated as before[1]; those of $x_e$ were calculated from $K_3 = K_h/K_a$, where $K_h$ is the hydrolysis constant of chlorine ($K_h = 2.23 \times 10^{-4}$)[4,1] and $K_a$ the dissociation constant of acetic acid ($K_a = 1.74 \times 10^{-5}$).[5a] (An equilibrium of the type of reaction 3 may be assumed to be unaffected by changes of the ionic strength. We therefore used the thermodynamic equilibrium constants for the calculation.)

TABLE I

DETAILS OF EXPERIMENTS CARRIED OUT IN THE PRESENCE OF ACETATE, OR ACETATE AND ACETIC ACID

| No. | $[HAc]_0$ Millimole/l. | $[Ac^-]_0$ Millimole/l. | $a$ Millimole/l. | $x_0$ Millimole/l. | $x_e$ Millimole/l. | $k^*$ sec.$^{-1}$ | "$k_{Ac^-}$" $\times 10^{-2}$ mole$^{-1}$ l. sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | 541 | 96 | 69.1 | 17.3 | 63.5 | 46 | 5.80 |
| 2 | 242 | 96.4 | 35.3 | 12.7 | 34.6 | 51 | 6.10 |
| 3 | 129.5 | 121 | 39.7 | 13.2 | 39.7 | 70 | 6.50 |
| 4 | 105 | 99 | 35.4 | 12.6 | 35.1 | 63 | 6.80 |
| 5 | 88 | 76 | 49.0 | 14.9 | 48.1 | 41 | 6.90 |
| 6 | 63 | 51.5 | 54.6 | 15.2 | 48.4 | 25 | 6.65 |
| 7 | 0 | 118 | 54.0 | 15.2 | 53.8 | 85 | 10.00 |
| 8 | 0 | 91.2 | 55.8 | 15.8 | 55.8 | 52 | 7.85 |
| 9 | 0 | 66.5 | 37.9 | 13.3 | 37.9 | 55 | 10.30 |
| 10 | 0 | 45.0 | 45.6 | 14.6 | 42.8 | 24 | 7.90 |
| 11 | 0 | 0 | 60.0[a] | 15.6[a] | 22.2[a] | 5.6[a] | ... |

[a] Mean value[1] of 5 experiments.

The values of $x$ were calculated from the measured values of $\Delta T$ from the following considerations. Immediately after mixing, the hydrogen ions present in the chlorine water will be neutralized by the acetate. This causes an initial temperature change $\Delta T_0$ which is given by the expression

$$\Delta T_0 = -(\Delta H_a/C_p)x_0$$

where $C_p$ is the specific heat of the solution, and $\Delta H_a$ is the heat of neutralization of $H^+$ by $Ac^-$ ($\Delta H_a = -0.46$ kcal. mole$^{-1}$, calculated from the change of $pK_a$ with temperature).[5a] At time $t$ we have therefore

$$x = x_0 - \frac{C_p}{\Delta H}\left(\Delta T_t + \frac{\Delta H_a}{C_p}x_0\right)$$

where $\Delta H$ is the heat of reaction of reaction 3. Now, $\Delta H$ can be calculated in two ways: (a) it is equal to $\Delta H_a$ plus the heat of hydrolysis of chlorine. The latter quantity[4] is equal to $\Delta H_h = 6.55$ kcal. mole$^{-1}$; (b) it can be calculated from our own experimental data, *viz.*

$$\Delta H = -\frac{\Delta T_\infty - \Delta T_0}{x_e - x_0} \times C_p$$

The results of methods (a) and (b) were in reasonable agreement, but method (b) usually yielded a slightly higher result (up to 3%). (Values of $C_p$ between 0.98 to unity were used according to the concentration of the solution.[6]) The latter value was employed for the calculation of $x$, in order to get consistent results. (We suspected that the discrepancy might be due to the heat of dilution of the acetate solution; we therefore measured this quantity in our apparatus, but found it negligibly small.)

In column 7 of the table, we report the specific rate with respect to chlorine, defined by the expression

$$k^* = -\mathrm{d}\ln(a - x)/\mathrm{d}t \qquad \text{(I)}$$

Although this quantity was found to decrease in the course of every run, it gives a useful indication of the reaction rate. The *initial* values are reported. (The change of $k^*$ can be seen from Fig. 1, which is a typical plot of log ($a - x$) *vs.* time.) For the sake of comparison, the mean value of $k^*$ for 5 experiments carried out in the absence of acetate[1] is also included (last row).

Column 8 is explained in the next section.

## Discussion

When the last row of Table I is compared with all the others, it becomes clear immediately that sodium acetate has a considerable accelerating influence on the rate of hydrolysis of chlorine. The fact that sodium perchlorate has no such influence shows that the effect of the acetate is not an "inert salt effect." We shall therefore assume that reaction 1 remains completely unaffected by the presence of acetate, and that in addition a reaction takes place whose rate depends on the acetate concentration. If we tentatively assume that this reaction is reaction 3, we get the rate equation

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(3) E. Giladi, A. Lifshitz and B. Perlmutter-Hayman, *Bull. Research Council Israel*, **8A**, 75 (1959).

(4) R. E. Connick and Yuan-tsan Chia, *J. Am. Chem. Soc.*, **81**, 1280 (1959).

(5) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, (a) p. 496; (b) p. 506.

(6) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., 35th Edition, 1954, p. 2105.

$$dx/dt = [k_{H_2O} + k_{Ac^-}([Ac^-]_0 - x)](a - x) - [k'_{H_2O}[H^+] + k'_{Ac^-}([HAc]_0 + x)]x^2 \quad (II)$$

where $[Ac^-]_0$ and $[HAc]_0$ are the concentrations of acetate and acetic acid which would correspond to $x = 0$, and $k$ and $k'$ refer to the forward and back reactions, respectively. On this tentative assumption, the meaning of $k^*$ as defined by equation I becomes (as long as the back reaction can be neglected)

$$k^* = k_{H_2O} + k_{Ac^-}([Ac^-]_0 - x) \quad (Ia)$$

The values of $k_{Ac^-}$ have to be evaluated by trial and error. The method—which also takes the back reaction into account—is described in detail in the Appendix. The values obtained were constant during each run (see Fig. 4, which is explained in the Appendix).

The results are shown in column 8 of Table I, under the heading "$k_{Ac^-}$." It can immediately be seen that the values do not correspond to a true constant.

A small increase with decreasing concentration of acetic acid can be noted. The high values of "$k_{Ac^-}$" obtained in the *absence* of acetic acid show that this increase, though almost within the limit of experimental error, is nevertheless significant. We therefore have to revise our previous tentative assumption about the reaction mechanism.

The possibility suggests itself that the retarding influence of acetic acid is due to its influence on the hydroxyl ion concentration, and that reaction 2 plays some role in the reaction scheme. Therefore we shall assume that all three reactions (1, 2 and 3) contribute to the observed rate. The meaning of $k^*$ then becomes

$$k^* = k_{H_2O} + k_{Ac^-}([Ac^-]_0 - x) + k_{OH^-}[OH^-] \quad (Ib)$$

The next step is the calculation of $[OH^-]$. As already discussed in the case of bromine,[2] reaction 2 cannot proceed faster than the hydroxyl ion (whose initial concentration is minute) can be supplied in the reacting system. The rate of autoprotolysis of water is far too slow[7] to sustain an appreciable percentage of the observed rate of up to 2.5 mole l.$^{-1}$ sec.$^{-1}$. Reaction 2 must therefore be preceded by the reaction

$$H_2O + Ac^- \rightleftarrows HAc + OH^- \quad (4)$$

Whereas an equilibrium of this type usually can be assumed to be attained "instantaneously" we cannot make this assumption in the present case: As far as we are aware, the rate of reaction 4 has not been measured. We may assume the back reaction to be diffusion controlled, with $k_4' \approx 6 \times 10^{10}$ sec.$^{-1}$. This shows that $k_4 \approx 10$ sec.$^{-1}$, so that at our concentration of acetate, $OH^-$ can be supplied by reaction 4 at a maximum rate of about 1 mole l.$^{-1}$ sec.$^{-1}$. This is of the same order of magnitude as the measured rate of disappearance of chlorine. Therefore, if we assume an at all appreciable percentage of this disappearance to be due to reaction 2, we find that equilibrium 4 is probably *disturbed* by this reaction. We can then calculate the hydroxyl ion concentration by treating reactions 4 and 2 as a system of *consecutive reactions*.

Since the concentrations of all the other participants are always much higher than that of $OH^-$, the latter can be calculated from the steady-state hypothesis which yields

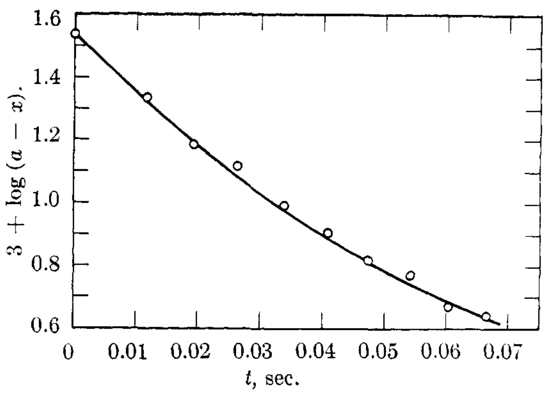

Fig. 1.—The dependence of log $(a - x)$ on time, for a typical experiment (run 5). The slope of this line is equal to $k^*$ as defined by equation I, and is seen to decrease as the reaction proceeds.

$$[OH^-] = \frac{K_W\{[Ac^-]_0 - x + (\alpha K_a/K_h)x^2\}}{K_a\{[HAc]_0 + x + \alpha(a - x)\}} \quad (III)$$

where $\alpha$ is defined by $\alpha = k_{OH}/k'_4$.

The value of $\alpha$ can only be guessed. Since $k'_4$ may be assumed to correspond to a diffusion controlled reaction, $\alpha$ cannot be a large quantity. If it were negligibly small, the value of $[OH^-]$ would of course become equal to the equilibrium value. A rough estimate shows, however, that if reaction 2 is to make an appreciable contribution to the measured rate of disappearance of chlorine, then—because of the extremely low concentration of $OH^-$—$k_{OH^-}$ must be very high and possibly *also* correspond to a diffusion controlled reaction. The value of $\alpha$ is therefore probably of the order of unity. This consideration shows that the third member in the numerator of expression III is negligibly small, *i.e.*, in calculating $[OH^-]$ we can neglect the back reaction 2 and get

$$[OH^-] = \frac{K_W([Ac^-]_0 - x)}{K_a\{[HA]_0 + x + \alpha(a - x)\}} \quad (IIIa)$$

An inspection of this expression shows that in spite of our lack of a precise knowledge of $\alpha$, we can make a fairly safe estimate of $[OH^-]$ when $[HAc]_0 > 0$, and may be widely in error when $[HAc]_0 = 0$. We shall therefore use only experiments 1–6 for the evaluation of $k_{Ac^-}$. Our calculation will become simplest if we assume $\alpha = 1$. We then get

$$k^* = k_{H_2O} + \left\{k_{Ac^-} + k_{OH^-}\frac{K_W}{K_a}\frac{1}{[HAc]_0 + a}\right\}([Ac^-]_0 - x) \quad (Ic)$$

and comparison with Ia shows the meaning of "$k_{Ac^-}$" to be

$$\text{“}k_{Ac^-}\text{”} = k_{Ac^-} + k_{OH^-}\frac{K_W}{K_a}\frac{1}{[HAc]_0 + a} \quad (IV)$$

*i.e.*, on this simplifying assumption the order with respect to both chlorine and acetate is the same as in the absence of any contribution by reaction 2.

In order to evaluate the rate constants $k_{Ac^-}$ and $k_{OH^-}$ we plotted "$k_{Ac^-}$" *vs.* $1/([HAc]_0 + a)$ (see Fig. 2). It is possible to draw a straight line through these points, which can be extrapolated to 1/

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(7) M. Eigen, *Disc. Faraday Soc.*, **17**, 194 (1954).

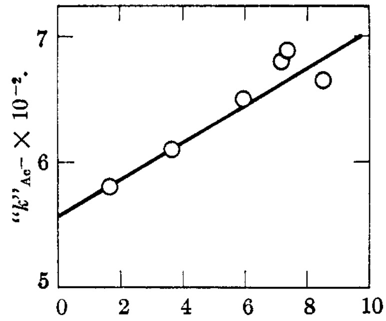

Fig. 2.—The values of "$k_{Ac^-}$" against the reciprocal of $([HAc]_0 + a)$, for experiments 1 to 6 (see equation IV).

$([HAc]_0 + a) = 0$, *i.e.*, $[OH^-] = 0$. This yields

$$k_{Ac^-} = 5.55 \times 10^2 \text{ mole}^{-1} \text{ l. sec.}^{-1}$$

It should be stressed that although there may be some uncertainty as to best straight line to be drawn, the extrapolation is so short that the value of $k_{Ac^-}$ would not be seriously affected if the line were drawn somewhat differently. This is a natural consequence of the fact that reaction 2 evidently contributes only a comparatively small correction term so that the value of $k_{Ac^-}$ obtained by extrapolation is not very much lower than the lowest measured values of "$k_{Ac^-}$." For the same reason, any error which may have been introduced by arbitrarily assuming $\alpha$ to be unity cannot be serious.

The situation is much less favorable with respect to $k_{OH^-}$. This constant can be obtained from the slope of Fig. 2. Using[5b] $K_W = 0.292 \times 10^{-14}$ we get $k_{OH^-} = (9 \pm 2)\ 10^{10}$, but this can only be considered an approximate value, because our assumption about $\alpha$ is a rather drastic one, and also because the slope is very sensitive to small errors in "$k_{Ac^-}$." It is not surprising that it should be difficult to evaluate $k_{OH^-}$ with any precision from experiments in which the contribution of reaction 2 is at most 15%. At first sight, it would seem more promising to evaluate $k_{OH^-}$ from the experiments where the relative contribution of reaction 2 is largest, *i.e.*, from the experiments carried out in the absence of acetic acid. However, it is just in these experiments that the value of $[OH^-]$ is most affected by small errors in the initial chlorine concentration, and—more important—by our lack of knowledge of $\alpha$. (The situation is particularly unsatisfactory because of the fact that if we assume $\alpha > 1$, *i.e.*, $k_{OH^-} > k_4$, $[OH^-]$ gets smaller, and $k_{OH^-}$ gets correspondingly larger. In other words, *assuming* a very high value of $k_{OH^-}$ *leads* to a very high value of $k_{OH^-}$, and *vice versa.*) Furthermore, equation IIIa shows that when $[HAc]_0 = 0$, the relative contribution of $OH^-$ either increases or decreases perceptibly as the reaction proceeds, unless $\alpha$ is *exactly* unity. Therefore, "$k_{Ac^-}$" may also either increase or decrease, although to a much lesser extent. No such change was observed. Still, it is possible that the value of "$k_{Ac^-}$" obtained for each experiment represents in reality only a mean value over the range of $x$ measured. This possibility somewhat detracts from the experimental reliability of reactions 7 to 10. It should also be mentioned that whatever our assumption about $\alpha$, we cannot explain why the rate constant in experiment 7 is so much higher than in experiment 10. Since in the former run $a$ is higher than in the latter, equations IIIa and IV would lead us to expect the opposite. Unless this is due to experimental error and the uncertainties described above, an additional factor must be operative in the absence of acetic acid, which we have not yet taken into account.

For all these reasons we cannot utilize the experiments carried out in the absence of acetic acid for the calculation of a more accurate value of $k_{OH^-}$, and have to content ourselves with the very approximate value given above. This value shows reaction 2 to be diffusion controlled. The rate constant even seems unusually high, but in view of the high mobility of the hydroxyl ion, not prohibitively so.

The assumption that reactions 1, 2 and 3 all contribute to the observed rate thus explains all our data, and gives reasonable values of the rate constants involved.

However, the high values of $k_{OH^-}$ lead to an inconsistency with the observed rate of exchange of radioactive chlorine between HOCl and $Cl^-$.[8] In spite of this, we believe that the evidence of reactions 1 to 6, and 7 to 10, taken *together*, shows that reaction 3 *alone* cannot explain our results. An additional reaction must always make a certain contribution; the increase of this contribution with decreasing acidity seems inevitably to point to reaction 2. But if at these very low concentrations of $OH^-$ (0.2 to 2.0 × $10^{-10}$ mole $l.^{-1}$) this reaction is to make an appreciable contribution, it must have the high rate constant found by us. The plausibility of this value of $k_{OH^-}$ will be further discussed in a later paper.

It might be added that of course reaction 2 *alone* cannot explain the observed rate. Firstly, the hydroxyl ions cannot be supplied fast enough. Secondly, the values of $k_{OH^-}$ would be impossibly high, and would vary from one experiment to the other ($k_{OH^-} = 2 \times 10^{12}$ and $2 \times 10^{11}$, for experiments 1 and 10, respectively). Thirdly, such an assumption is contradicted by the straight line obtained in Fig. 2, which cuts the "$k_{Ac^-}$" axis at a value very different from zero.

## Appendix

**Calculation of $k_{Ac^-}$.**—When the back reaction in the hydrolysis of chlorine is neglected, equation II is easily integrated and yields

$$\frac{1}{k_{H_2O}/k_{Ac^-} + [Ac^-]_0 - a} \times L(x) + \text{const.} = k_{Ac^-}t \quad (V)$$

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(8) The rate of exchange of radioactive chlorine between $Cl^-$ and HOCl in alkaline solution was found by Anbar and co-workers (M. Anbar, S. Guttmann and R. Rein, *J. Am. Chem. Soc.*, **81**, 1816 (1959)) to follow the rate law: $v = k[H^+][HOCl][Cl^-]$ with $k \gg k'_{H_2O}$; the authors therefore assumed the exchange reaction to be different from reaction 1, and to take place *without* the formation of elementary chlorine. On the other hand, when elementary chlorine *is* formed in a reaction involving HOCl and $Cl^-$, we should certainly expect isotopic exchange to take place. Therefore, if reaction 2 is indeed as fast as we have found, it should compete with the above rate law at high values of $p$H, so that beginning at $p$H ~ 11, the rate of exchange should decrease with increasing $p$H far less steeply than was found experimentally. This inconsistency was pointed out to us by the Referee.

where $L$ $(x)$ is defined by

$$L(x) \equiv \ln \frac{k_{H_2O}/k_{Ac^-} + [Ac^-]_0 - x}{a - x} \qquad (VI)$$

Equation V is a transcendental function for the desired rate constant which must therefore be calculated by trial and error.

For this purpose, we first guessed a trial value from $k^*$, using suitable mean values of $x$ corresponding to the time intervals considered.

Inserting this trial value into VI we found a series of values of $L$, which we call $L^0$. These were plotted against time, from which we get

$$k^1{}_{Ac^-} = \frac{dL^0}{dt} \Big/ \left(\frac{k_{H_2O}}{k^0{}_{Ac^-}} + [A\bar{c}]_0 - a\right) \qquad (VII)$$

The new value $k^1{}_{Ac^-}$ is a better approximation to $k_{Ac^-}$ than $k^0{}_{Ac^-}$ had been. Whenever $k^0{}_{Ac^-}$ and $k^1{}_{Ac^-}$ differed at all significantly, the procedure was repeated, until the values of $k^n{}_{Ac^-}$ and $k^{n+1}{}_{Ac^-}$ in expression VII became identical.

That $k^1{}_{Ac^-}$ is indeed a better approximation than $k^0{}_{Ac^-}$ can be shown in the following way: Let us suppose that the first trial value $k^0{}_{Ac^-}$ differs from the true value of $k_{Ac^-}$ by an amount $\epsilon$ which is small in comparison with $k_{Ac^-}$. Expression VII can then be written

$$k^1{}_{Ac^-} = F(k^0{}_{Ac^-}) = F(k_{Ac^-} + \epsilon) \approx F_{Ac^-}(k_{Ac^-}) + \epsilon(dF/dk^0{}_{Ac^-}) = k_{Ac^-} + \epsilon\, k_{H_2O}/[k_{H_2O} + k^0{}_{Ac^-}([Ac^-]_0 - x)]$$

Since $dF/dk^0{}_{Ac^-}$ is always positive and smaller than unity we conclude that if, for instance, $k^0{}_{Ac^-}$ was too large, than $k^1{}_{Ac^-}$ will also be too large, but will be nearer to the true value.[9]

In most of our experiments, the back reaction cannot be neglected. The integrated form of equation II becomes cumbersome and not at all suitable for use in a trial and error method.

We therefore developed a device[10] which enables us to use an expression of the form of equation (V) where, however, the time $t$ is substituted by an empirical time scale $\theta$ which is "corrected" for the contribution of the back reaction.

Provided the equilibrium between $H^+$, $Ac^-$ and HAc can be assumed to be maintained during the reaction, equation II can be re-written in the form

$$\frac{dx}{dt} = [k_{H_2O} + k_{Ac^-}([Ac]_0 - x)](a - x)(1 - \varphi(x)) \qquad (IIa)$$

where

$$\varphi(x) = \frac{K_a}{K_h} \frac{x^2([HAc]_0 + x)}{(a - x)([Ac^-]_0 - x)} \qquad (VIII)$$

The expression $\varphi(x)$ represents the relative contribution of the back reaction, and can easily be calculated for every measured value of $x$. We found that when $\varphi(x)$ was plotted against the corresponding values of *time*, simple curves were obtained in all experiments, which with sufficient accuracy could be represented as short power series in time.

Figure 3 shows $\varphi$ as a function of time for a typical experiment. The circles correspond to the values calculated from expression VIII for 9 measured values of $x$, whereas the smooth line represents the analytical expression

$$\varphi(t) = 0.003 + 2.8t + 80t^2$$

in a range between zero and 0.045 sec. The fit is seen to be satisfactory.

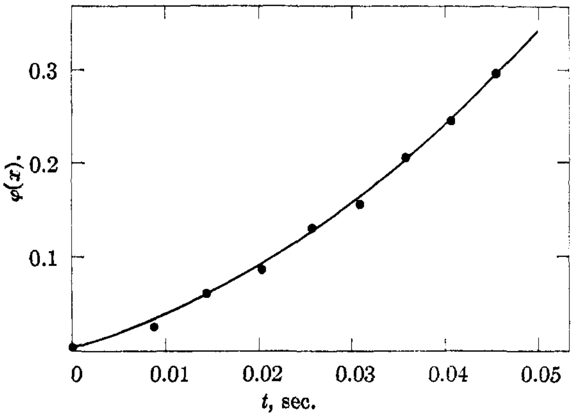

Fig. 3.—The value of $\varphi(x)$ as defined by equation VIII, against the corresponding values of time, for a typical experiment (run 1).

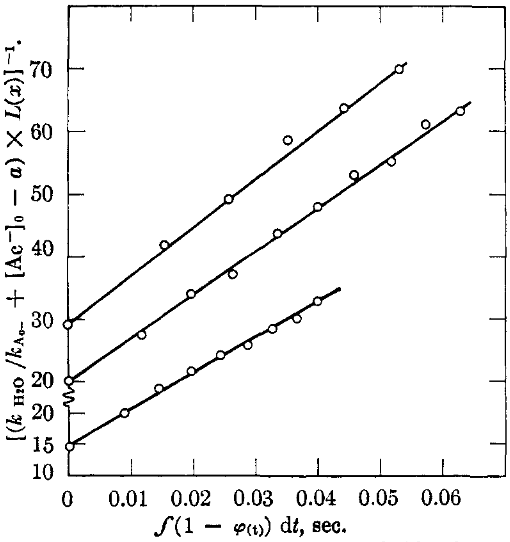

Fig. 4.—The dependence of the left-hand side of equation V on a time scale which has been corrected for the back-reaction, for three typical experiments (runs 1, 5 and 10). Straight lines correspond to constant values of the rate constant.

Equation IIa can now be written in the form

$$\frac{dx}{(a - x)(k_{H_2O}/k_{Ac^-} + [Ac^-]_0 - x)} = k_{Ac^-}[1 - \varphi(t)]dt \qquad (IIb)$$

This can be integrated easily. The result is identical with equation V, except that instead of $t$ there appears $\theta$, where

$$\theta \equiv \int_0^t [1 - \varphi(t)]dt$$

We used $\theta$ instead of $t$ in the trial and error method described above. Figure 4 shows plots of the left-hand side of equation V as a function of $\theta$ for three representative experiments. Straight lines are seen to be obtained.

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[9] The authors are indebted to Dr. H. J. G. Hayman for suggesting this test of their trial and error method.

[10] See A. Lifshitz and B. Perlmutter-Hayman, *Bull. Research Council Israel*, **9A**, 200 (1960), where the method is discussed in detail.