It is clear that the configuration and modes of attachment in the activated states in the formation and dissociation of this complex are not known. A knowledge of the factors influencing *syn-anti* isomerization in aliphatic ketoximes along with thermodynamic and kinetic studies on planar complexes containing bidentate ligands would help evaluate the activated states involved.

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[CONTRIBUTION FROM THE MAX-PLANCK-INSTITUT FÜR PHYSIKALISCHE CHEMIE, GOETTINGEN, GERMANY]

The Kinetics of Halogen Hydrolysis

BY MANFRED EIGEN AND KENNETH KUSTIN*

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By means of the temperature jump relaxation technique, the kinetics of hydrolysis of the halogens Cl_2, Br_2 and I_2 have been studied. The over-all process is fastest for Br_2 and slowest for Cl_2. Numerical values for the rate constants of the over-all reaction mechanism $X_2 + H_2O \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} X^- + H^+ + XOH$ could be determined. The measured values for the over-all hydrolysis rate constant $\overrightarrow{k}$ are: $\overrightarrow{k}_{Cl_2} = 11.0$ sec.$^{-1}$, $\overrightarrow{k}_{Br_2} = 110$ sec.$^{-1}$, $\overrightarrow{k}_{I_2} = 3.0$ sec.$^{-1}$. A general mechanism, in which hydrolysis occurs *via* the intermediate X_2OH^-, is proposed. From studies of *p*H and concentration dependence individual rate constants could be determined or estimated. General trends exhibited by the measured or estimated values are discussed.

Introduction

When the halogens Cl_2, Br_2 and I_2 are dissolved in pure water, the ensuing solution becomes acidic with production of the corresponding hypohalogen acid. The hydrolysis equilibrium, which can be formally written as

$$X_2 + H_2O \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} H^+ + X^- + XOH \qquad (I)$$

(where X = Cl, Br or I and $\overrightarrow{k}$ (sec.$^{-1}$) or $\overleftarrow{k}$ (M^{-2} sec.$^{-1}$), respectively, are over-all rate constants) has been the subject of intensive research for a long period of time. The solutions are generally unstable with respect to the formation of more highly oxidized species, but this process is relatively slow. It has therefore been possible to achieve an almost complete thermodynamic description of all the primary equilibria pertinent to these systems. A comparably complete kinetic description has been lacking because most of the reactions involved in the hydrolysis occur in times around or shorter than 10^{-3} sec. (An exception is exhibited by the over-all hydrolysis of chlorine which has been studied with flow techniques.) By the application of relaxation techniques, it has now become possible to observe directly the rates of hydrolysis of all three halogens and to analyze the above formal mechanism in terms of individual elementary steps.

It will prove useful for the evaluation of the results to summarize first the thermodynamic data and to review the most important attempts at kinetic measurements.

The equilibrium constant for reaction (I) in the case of chlorine had been well characterized by Jakowkin[1] as long ago as 1899. We have used the more inclusive values of Connick and Chia,[2] adjusted to 20° and ionic strength $\mu = 0.1$ M, however. The same authors also measured the heat of reaction (I). The stability constant of trichloride ion has been measured spectrophotometrically by Zimmermann and Strong.[3] Latimer[4] reviews the data for the protonic dissociation constant of ClOH. The over-all rate of hydrolysis of chlorine was first measured by Shilov and Soloduschenkov[5] and later confirmed by Lifschitz and Perlmutter-Hayman,[6a] who have extended the measurements to acetate buffer solutions.[6b]

For bromine the equilibrium constant as well as heat of reaction (I) has been definitively measured by Liebhafsky,[7] whose value we have used, applied to the conditions of our experiments. Latimer[4] reviews the literature with respect to tribromide ion formation and protonic dissociation constant of BrOH. An attempt was made by Lifschitz and Perlmutter-Hayman[8] to measure the rate of bromine hydrolysis using a flow method. They found attainment of equilibrium to be essentially complete within their shortest measurable time, 3.8 milliseconds.

The iodine system has probably been the subject of the most extensive measurement of all three halogens. The equilibrium constant and heat of reaction for reaction (I) has been most recently redetermined by Allen and Keefer[9] (*cf.* for previous literature) whose value, adjusted to our conditions, we have used. Awtrey and Connick[10] and Allen and Keefer[9] review the spectrophotometric data

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* Dept. of Chemistry, Brandeis University, Waltham 54, Mass.

(1) A. A. Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

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

(3) G. Zimmermann and F. C. Strong, *ibid.*, **79**, 2063 (1957).

(4) W. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

(5) R. A. Shilov and S. M. Soloduschenkov, *J. Phys. Chem. (U.S.S.R.)*, **19**, 405 (1945).

(6) (a) A. Lifschitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, **64**, 1663 (1960); (b) *ibid.*, **65**, 753 (1961).

(7) H. A. Liebhafsky, *J. Am. Chem. Soc.*, **61**, 3513 (1939).

(8) A. Lifschitz and B. Perlmutter-Hayman, *Bull. Res. Counc. of Israel*, **8A**, 166 (1959).

(9) T. L. Allen and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 2957 (1955).

(10) A. D. Awtrey and R. E. Connick, *ibid.*, **73**, 1842 (1951).

on I_2, I_3^- and IOH, and give the stability constant of the triiodide ion as well. Connick and Chia[11] have recently measured the protonic dissociation constant of IOH, and the stability of the I_2OH^- complex. Of special interest is the investigation of Bell and Gelles[12] on the halogen cations. They demonstrated: (1) the extreme unlikelihood of encountering $H_2O{\cdot}Cl^+$ or $H_2O{\cdot}Br^+$ in solution; (2) the presence of $H_2O{\cdot}I^+$ under certain conditions. Some early attempts to measure the hydrolysis of I_2 indirectly were demonstrated by Liebhafsky[13] to be fallacious, leading to inconsistent rate constants.

Finally, we should like to call attention to the isotope exchange measurements of the hypohalites in alkaline solution by Anbar and Taube[14] and Anbar, Guttmann and Rein,[15] where the role of Br_2OH^- and Cl_2OH^- as possible intermediates is mentioned.

TABLE I

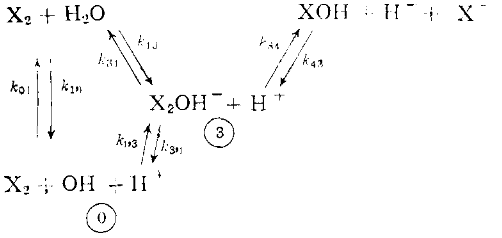
THERMODYNAMIC EQUILIBRIUM CONSTANTS

Reaction	Equilibrium constant	Ref.
	$K_{\text{hydr.}} = \frac{a_{X^-}\, a_{H^+}\, a_{XOH}}{a_{X_2}}$	
$Cl_2 + H_2O \rightleftarrows Cl^- + H^+ + ClOH$	$3.88 \times 10^{-4\,a}$	(2)
$Br_2 + H_2O \rightleftarrows Br^- + H^+ + BrOH$	$4.46 \times 10^{-9\,a}$	(7)
$I_2 + H_2O \rightleftarrows I^- + H^+ + IOH$	$4.3 \times 10^{-13\,a}$	(9)
	$K_{X_3^-} = \frac{a_{X_3^-}}{a_{X_2}\, a_{X^-}}$	
$Cl_2 + Cl^- \rightleftarrows Cl_3^-$	0.18^b	(3)
$Br_2 + Br^- \rightleftarrows Br_3^-$	17^b	(4)
$I_2 + I^- \rightleftarrows I_3^-$	830^a	(10)
	$K_{XOH} = \frac{a_{H^+} a_{X^-}}{a_{XOH}}$	
$ClOH \rightleftarrows H^+ + ClO^-$	$3.2 \times 10^{-8\,b}$	(4)
$BrOH \rightleftarrows H^+ + BrO^-$	$2 \times 10^{-9\,b}$	(4)
$IOH \rightleftarrows H^+ + IO^-$	$2.3 \times 10^{-11\,b}$	(11)
$IO^- + I^- + H_2O \rightleftarrows I_2OH^- + OH^-$	$K_{I_2OH^-} = \frac{a_{I_2OH^-} a_{OH^-}}{a_{IH^-} a_{I^-}} = 0.13^b$	(11)
$H_2O + I_2 \rightleftarrows H_2O{\cdot}I^+ + I^-$	$K_{H_2O\cdot I^+} = \frac{a_{H_2O\cdot I^+} a_{I^-}}{a_{I_2}} = 1.2 \times 10^{-11\,b}$	(12)

[a] Temp. 293 °K. [b] Temp. 298 °K.

General Mechanism.—In order to facilitate a complete understanding of the results, we begin by presenting the most complete mechanism, including all possible steps. After deriving the corresponding rate equations and relaxation times, it will be shown that it is possible to make some *a posteriori* decisions about the probable mechanism.

Consider the following mechanism



(11)

It can be shown (*cf.* below) that under the conditions of the experiments $H_2O{\cdot}X^+$, X_2OH^- and OH^- are always present at such small concentrations that for the states ⓪, ② and ③ the steady state assumption can be applied

$$\frac{d(OH^-)}{dt} = 0 = k_{10} + k_{30}(X_2OH^-) - k_{01}(H^+)(OH^-) - k_{03}(X_2)(OH^-) \quad (1)$$

$$(OH^-) = \frac{k_{10} + k_{30}(X_2OH^-)}{k_{01}(H^+) + k_{03}(X_2)} \quad (2)$$

$$\frac{d(X_2OH^-)}{dt} = 0 = k_{03}(OH^-)(X_2) + k_{43}(XOH)(X^-) + k_{13}(X_2) - k_{30}(X_2OH^-) - k_{31}(X_2OH^-)(H^+) - k_{34}(X_2OH^-) \quad (3)$$

$$(X_2OH^-) = \frac{[k_{03}(OH^-) + k_{13}]\,(X_2) + k_{43}(XOH)(X^-)}{k_{30} + k_{31}(H^+) + k_{34}} \quad (4)$$

(X_2OH^-) can be written in a more convenient form

$$(X_2OH^-) = \frac{k_{13}'(X_2) + k_{43}(XOH)(X^-)}{k_{34} + k_{31}'(H^+)} \quad (5)$$

by substituting (2) into (4) and using the definitions

$$k_{13}' = k_{13} + \frac{k_{03}k_{10}}{k_{01}(H^+) + k_{03}(X_2)} \quad (6)$$

$$k_{31}' = k_{31} + \frac{k_{30}k_{01}}{k_{01}(H^+) + k_{03}(X_2)} \quad (7)$$

For $(H_2O{\cdot}X^+)$ we obtain

$$\frac{d(H_2O{\cdot}X^+)}{dt} = 0 = -k_{24}(H_2O{\cdot}X^+) - k_{21}(H_2O{\cdot}X^+)(X^-) + k_{42}(XOH)(H^+) + k_{12}(X_2) \quad (8)$$

$$(H_2O{\cdot}X^+) = \frac{k_{42}(XOH)(H^+) + k_{12}(X_2)}{k_{24} + k_{21}(X^-)} \quad (9)$$

The over-all rate equation may now be written

$$\frac{d(X_2)}{dt} = \frac{-k_{12}k_{24}(X_2)}{k_{24} + k_{21}(X^-)} - \frac{k_{13}'k_{34}(X_2)}{k_{34} + k_{31}'(H^+)} + \frac{k_{42}k_{21}(XOH)(H^+)(X^-)}{k_{24} + k_{21}(X^-)} + \frac{k_{43}k_{31}'(XOH)(H^+)(X^-)}{k_{34} + k_{31}'(H^+)} \quad (10)$$

after substitution of the steady state equations.

To obtain the relaxation time for the equilibration between state ① and ④ we make use of these definitions or conditions[16]

$$(X_2) = (\overline{X}_2) + \delta(X_2);\ \text{etc. for } (X^-),\ (XOH),\ (H^+) \quad \text{(i)}$$

$$\delta(X_2) \ll (\overline{X}_2);\ \text{etc. for } (X^-),\ (XOH),\ (H^+) \quad \text{(ii)} \quad (11)$$

$$-\delta(X_2) = \delta(XOH) = \delta(H^+) = \delta(X^-) \quad \text{(iii)}$$

$$K_{XOH} = \frac{\overrightarrow{k}}{\underleftarrow{k}} = \frac{(\overline{XOH})(\overline{X}^-)(\overline{H}^+)}{(\overline{X}_2)} \quad \text{(iv)}$$

The symbol (X_2) represents the instantaneous concentration, $(\overline{X}_2)$ is the (time independent) equilibrium concentration, and $\delta(X_2)$ is a (time dependent) small deviation from equilibrium. The conditions (11), applied to eq. 10 yield, after expansion

$$\frac{d[\delta(X_2)]}{dt} = \frac{-(\delta X_2)}{\tau} \quad (12a)$$

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(11) R. E. Connick and Yuan-tsan Chia, University of California Radiation Laboratory-8311 (*cf.* Y. Chia, Thesis, June 2, 1958).

(12) R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).

(13) H. A. Liebhafsky, *Z. physik. Chem.*, **155A**, 289 (1931).

(14) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **80**, 1073 (1958).

(15) M. Anbar, S. Guttmann and R. Rein, *ibid.*, **81**, 1816 (1959).

(16) M. Eigen, *Discussions Faraday Soc.*, **24**, 24 (1957).

with $1/\tau =$

$$\frac{k_{12}k_{24} + k_{42}k_{21}\{(\mathrm{X\bar{O}H})(\mathrm{\bar{H}^+}) + (\mathrm{X\bar{O}H})(\mathrm{\bar{X}^-}) + (\mathrm{\bar{X}^-})(\mathrm{H^+})\}}{k_{21}(\mathrm{\bar{X}^-}) + k_{24}} +$$
$$\frac{k_{13}'k_{34} + k_{43}k_{31}'\{(\overline{\mathrm{XOH}})(\mathrm{\bar{H}^+}) + (\overline{\mathrm{XOH}})(\mathrm{\bar{X}^-}) + (\mathrm{\bar{X}^-})(\mathrm{\bar{H}^+})\}}{k_{31}'(\mathrm{\bar{H}^+}) + k_{34}}$$
$$= \overrightarrow{k} + \overleftarrow{k}\,\{(\overline{\mathrm{XOH}})(\mathrm{\bar{H}^+}) + (\overline{\mathrm{XOH}})(\mathrm{\bar{X}^-}) + (\mathrm{\bar{X}^-})(\mathrm{\bar{H}^+})\} \quad (12b)$$

The relaxation time τ can be directly measured under suitable conditions. The boundary condition for (12a) with $\overline{\mathrm{X}}_2$ = const. is simply $\delta[\mathrm{X}_2]$ = const. It is applicable to the stepwise change of equilibrium as involved in the T-jump relaxation experiment (*cf.* below).

From the results of Bell and Gelles[12] we may rule out pathway ① → ② → ④ for all three halogens, since the species $[\mathrm{H_2O{\cdot}I^+}]$ and especially $[\mathrm{H_2O{\cdot}Br^+}]$ and $[\mathrm{H_2O{\cdot}Cl^+}]$ are present to too small an extent. We may, however, examine the probability of such a mechanism for I_2, under consideration of the measured equilibrium constants, the measured relaxation time (τ = 1.2 msec. depending to a slight degree upon concentration and *p*H) and knowledge of the magnitudes of the "diffusion controlled" reaction rate constants.[17]

In the experiments, the sum of the concentration product terms (bracket terms) in (12b) was approximately 2×10^{-10} M. If reaction ② → ① is diffusion controlled, then k_{21} has the order of magnitude of 10^{10} M^{-1} sec.$^{-1}$. Similarly, a diffusion controlled reaction ④ → ② would, at best, yield a rate constant of the order $k_{42} \approx 5 \times 10^9$ M^{-1} sec.$^{-1}$. From the measured equilibrium values we know K_{12} and K_{24} and may thereby estimate the remaining rate constants. We have, $K_{12} = 1.2 \times 10^{-11}\ M = k_{12}/k_{21}$; thus, $k_{12} \approx 1 \times 10^{-1}$ sec.$^{-1}$. Likewise, $K_{24} = K_{\mathrm{IOH}}/K_{12} = 4 \times 10^{-2} = k_{24}/k_{42}$; thus, $k_{24} \approx 2 \times 10^7$ sec.$^{-1}$. We arrive then at the upper limit values

$$k_{21}(\mathrm{I^-}) \approx 5 \times 10^4 \text{ sec.}^{-1} \text{ for } [\mathrm{I^-}] = 5 \times 10^{-6}\ M$$
$$k_{24} \approx 2 \times 10^7 \text{ sec.}^{-1}$$
$$k_{24} \gg k_{21}(\mathrm{I^-})$$

from which we obtain, for ① → ② → ④

$$\frac{1}{\tau} = k_{12} + \frac{k_{42}}{k_{24}} \cdot k_{21}\{(\mathrm{I\bar{O}H})(\mathrm{\bar{H}^+}) + (\mathrm{I\bar{O}H})(\mathrm{\bar{I}^-}) + (\mathrm{\bar{I}^-})(\mathrm{\bar{H}^+})\} \quad (13)$$

From $K_{\mathrm{IOH}} = 5.8 \times 10^{-13}\ M^2$ we know that

$$k_{12} \ll \frac{k_{42}}{k_{24}} k_{21}\{(\overline{\mathrm{HOI}})(\mathrm{\bar{H}^+}) + (\overline{\mathrm{HOI}})(\mathrm{\bar{I}^-}) + (\mathrm{\bar{H}^+})(\mathrm{\bar{I}^-})\}$$

and obtain $[1/\tau]$ ① → ② → ④ = 50 sec.$^{-1}$. The experimentally determined value, however, amounts to

$$[1/\tau] = 870$$

Thus, one would have to assume a k_{21} value more than 10 times as high as one which is valid for a diffusion controlled reaction, which is physically impossible.

All the assumptions we have made lead to the largest possible value for $(k_{42}/k_{24})\, k_{21}\{(\overline{\mathrm{IOH}})(\mathrm{\bar{H}^+}) + (\overline{\mathrm{IOH}})(\mathrm{\bar{I}^-}) + (\mathrm{\bar{I}^-})(\mathrm{\bar{H}^+})\}$ under exclusion of path ① → ③ → ④. Therefore, we may conclude that the major part of the reaction does not take place *via* ① → ② → ④. All conclusions made for the reaction of I_2 hold even more for the reactions of Br_2 and Cl_2, since in these cases the quantity k_{42}/k_{24} is still much smaller than for I_2.

Hereafter, we can refer the measured relaxation times to the mechanism

$$\begin{tikzcd} \textcircled{1} \arrow[dd] \arrow[dr] & & \\ & \textcircled{3} \arrow[r] & \textcircled{4} \\ \textcircled{0} \arrow[ur] & & \end{tikzcd}$$

only (*cf.* Results). In addition, we shall omit in the following the (¯) superscript, since all measured concentrations refer to the equilibrium state.

Experimental

The experiments were carried out by means of the T-jump relaxation method which is described elsewhere.[18] The temperature rise to perturb the chemical system occurs within 5×10^{-7} sec., and amounts to about 10°. Since cells with platinized brass electrodes showed some iodine decomposition after passage of the high voltage pulse, cells with solid gold electrodes were used throughout. In these cells, the solutions were completely stable over the whole course of the experiments. The shift of equilibrium initiated by the T-jump was followed spectrophotometrically.

The substances used were of reagent grade quality. Riedel de Haen iodine was resublimed several times according to the procedure of Kolthoff and Belcher.[19] No stock solution was used, the samples were prepared from weighed out portions of the repurified iodine. The calculated I_3^- absorbancy was in good agreement with the measured value. This type of measurement constitutes direct proof of the purity and stability of a solution. Since I_2 was present at the relatively high concentration of 10^{-3} M, I_3^-, which can be determined quantitatively from its absorbancy, is a direct measure of the concentration of I^- (both around 5×10^{-6} M). From the stoichiometry (and assuming no further reaction), $(\mathrm{I^-}) + (\mathrm{I_3^-})$ must equal (IOH). Therefore, analysis of I_3^- provides a very sensitive test of the hydrolysis, and any decomposition of I_2 in which I^- is produced. Since H^+ also arises stoichiometrically in the hydrolysis, *p*H measurements allow some further checking of the composition. These additional determinations were in good agreement with the spectrophotometric results.[20a]

Riedel de Haen liquid bromine was shaken three times with separate portions of conductivity water, then a sample was drawn off and dissolved in fresh conductivity water to prepare the stock solution: $[\mathrm{Br_2}] = 1.13 \times 10^{-2}$ M. Concentrations were determined by titrating an equivalent amount of iodine ($\mathrm{Br_2 + 2\ I^- \rightarrow I_2 + 2\ Br^-}$) with tetrathionate. The concentrations thus determined were checked against *p*H measurements made with a glass electrode. Any deviations were within experimental limits.

A stock solution of chlorine was prepared by passing high quality (commercially available) chlorine gas through conductivity water. The stock solution was immediately titrated (as in the case of Br_2) and sample solutions were made directly thereafter. The titration results were checked with *p*H measurements, with good agreement. No chlorine stock solution was kept for more than 4 or 5 hr.

The mode of detection makes use of the light absorption of the halogen species in solution. In the case of iodine,

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[17] M. Eigen, *Z. phys. Chem.*, *N. F.*, **1**, 176 (1954), and *Z. Elektrochem.*, **64**, 115 (1960); M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **82**, 5952 (1960).

[18] G. Czerlinski and M. Eigen, *Z. Elektrochem.*, **63**, 652 (1959), M. Eigen and L. De Maeyer, in Vol. VIII of "Technique of Organic Chemistry," Ed. A. Weissberger, 2nd Ed., Interscience Publishers, Inc., New York, N. Y.

[19] I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, p. 220.

[20] (a) We gratefully acknowledge the kind assistance in this part of the work by Dr. G. v. Bünau (*cf.* also G. v. Bünau and M. Eigen, *Z. phys. Chem. N.F.*, in press). (b) O. E. Myers, *J. Chem. Phys.*, **28**, 1027 (1958). We wish to point out that the reported value for the rate constant $\mathrm{I_2 + I^- \xrightarrow{k_R} I_3^-}$, $k_R = 4 \times 10^{10}$ M^{-1} sec.$^{-1}$ seems to be too high for a diffusion controlled reaction of this charge type. Theoretical calculations lead to a maximum value $<10^{10}$ M^{-1} sec.$^{-1}$

changes in the absorbancy (at 350 mμ) of the small amount of I_3^- present was used to determine the relaxation time. Two relaxation times are present. The first, due to the equilibrium $I_2 + I^- \rightleftarrows I_3^-$, is several orders of magnitude shorter than that of the hydrolytic reaction.[20b] The second relaxation time is the one represented by (12b), where, however, the completed equilibrium of I_3^- has to be taken into account ($-\delta[I_2] = \delta[IOH] = \delta[H^+] = \delta[I^-] + \delta[I_3^-]$). It turns out that the *relative* change of I_3^- reflects the extent of hydrolysis. For bromine, light absorption at 400 mμ was directly used, and for chlorine, absorption at 360 mμ. Here the X_2 concentrations are comparable to or smaller than those of the hydrolyzed species so that X_2 is sensitive to equilibrial changes. No buffers or indicators were used; thus, the experiments record only the hydrolysis in pure water. There is no catalysis present, unless engendered by species involved in the equilibria.

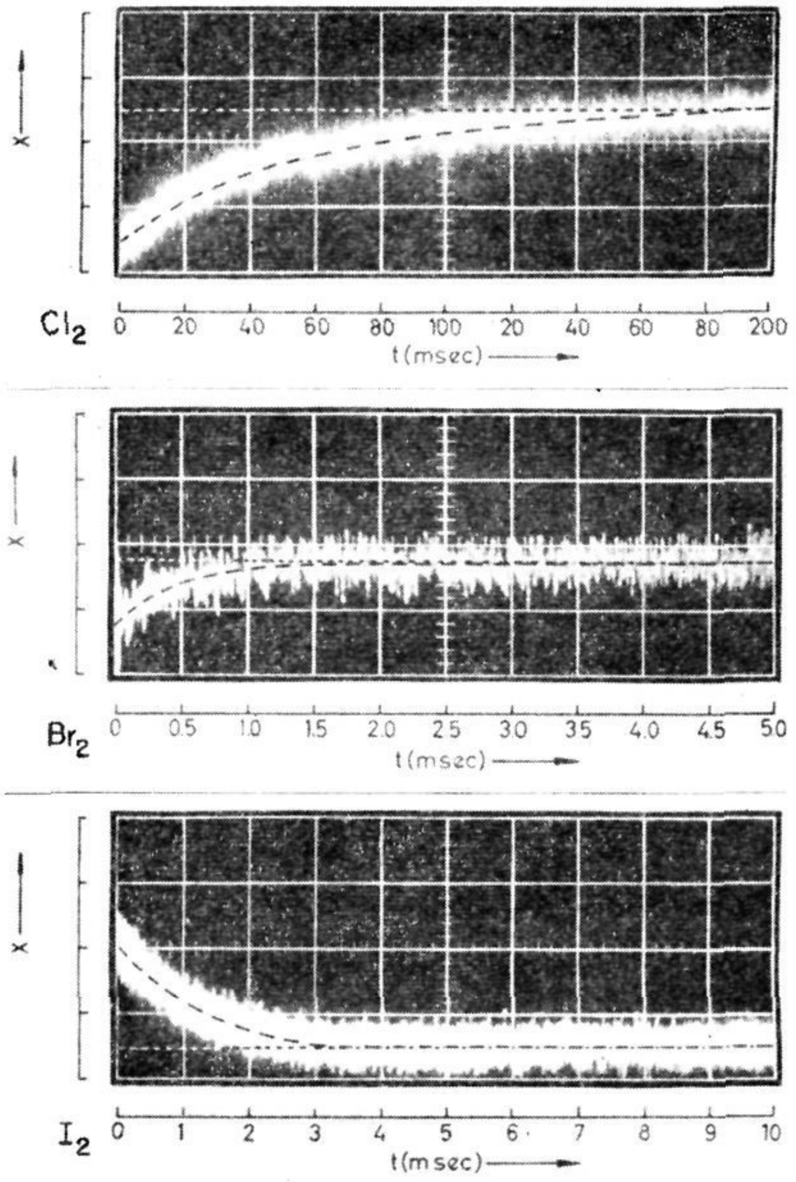

Fig. 1.—Oscillograms of T-jump relaxation experiments. (a) $(Cl_2)_0 = 2.92 \times 10^{-2}$ *M*, τ = 57 msec. (b) $(Br_2)_0 = 2.26 \times 10^{-3}$ *M*, τ = 0.35 msec. (c) $(I_2)_0 = 1.0 \times 10^{-3}$ *M*, τ = 1.2 msec. In traces (a) and (b), *x* was measured by means of the Cl_2 or Br_2 absorbancy directly. Increasing *x* means decreasing absorption and therefore disappearance of Cl_2 or Br_2, respectively. This behavior reflects the known temperature dependence of the hydrolysis equilibrium; *i.e.*, a decrease of the halogen concentration (Cl_2, Br_2, I_2) with increasing temperature. In trace (c) the measured parameter is the I_3^- absorbancy. The initial (instantaneous) increase of *x* is due to dissociation of I_3^- into I_2 and I^- with increasing temperature (*cf.* ref. 10). The measured time process results again from the shift in the hydrolysis equilibrium. However, the I_3^- absorption here is sensitive to the relative change of I^- rather than to I_2, since the concentration of I^- is almost equal to that of I_3^-, but 100 times lower than that of I_2 (the relative change of which is almost negligible). Therefore, decreasing *x* means, again, a disappearance of I_2 (formation of I^- and I_3^-).

All measurements were made at ionic strengths of 0.1 *M* and equilibrium temperatures of 20°. Thermodynamic equilibrium constants were corrected, where necessary, by use of the appropriate activity coefficients. The accuracy of the experiments with iodine was limited by a slight electrolytic production of I^- which altered the concentration of I_3^- during the experiment. The limited solubility of iodine in water restricts, too, the extent to which the total iodine concentration could be varied. The rate constants for this system have the relative error of ± 10%. For bromine, the relative error is ± 3%. In the case of chlorine, the total sweep time was comparable to the onset time of convection in the cell and to lamp fluctuations. The uncertainty thus involved in evaluating the oscillograms is reflected in the error of ± 10%.

No attempt was made to study the hydrolysis of fluorine since the apparatus was not designed to handle F^-, and the competing, irreversible oxidation of water to oxygen, would render this type of experiment useless.

Results

Representative oscillograms of relaxation experiments with Cl_2, Br_2 and I_2 solutions are shown in Fig. 1. The ordinate *x* is in arbitrary units representative of the extent of reaction, and the abscissa *t* is time in milliseconds. The relaxation time τ is given by the time *t* after which a signal *x* has decayed to x/e; ($x = x_0 e^{-t/\tau}$).

The results obtained with the three systems will be discussed separately in the following sections.

(a) **Chlorine.**—Figure 2 shows the effect of the concentration product and *p*H on the relaxation time. The ordinate intercept is equal to $\overrightarrow{k}$, and the slope is $\overleftarrow{k}$. The quotient of the ordinate intercept and the slope should yield the concentration equilibrium constant, thus constituting an independent check on the validity of the kinetic measurements and their attribution to the proposed mechanism.

The results for chlorine at 20° and μ = 0.1 *M* are

$$\overrightarrow{k} = 11.0 \text{ sec.}^{-1}$$

$$\overleftarrow{k} = 1.80 \times 10^4 \, M^{-2} \text{ sec.}^{-1}$$

$$K_{ClOH} = 6.0 \times 10^{-4} \, M^2$$

The values for $\overrightarrow{k}$, $\overleftarrow{k}$ and K_{ClOH} are in good agreement with those previously reported.[1,2]

The over-all rate constants and the constants for the individual steps in the mechanism are related in the following way

$$\overrightarrow{k} = \frac{k_{13}'k_{34}}{k_{31}'(H^+) + k_{34}} \qquad (14)$$

$$\overleftarrow{k} = \frac{k_{31}'k_{43}}{k_{31}'(H^+) + k_{34}} \qquad (15)$$

The exclusion of any dependence such as $1/\tau \propto \frac{\Sigma C_i^2}{(H^+)}$[21a] and the ideal concentration dependence giving the correct equilibrium constant yields the important inequality $k_{31}(H^+) \ll k_{34}$. Thus

$$\overrightarrow{k} = k_{13}'; \; \overleftarrow{k} = k_{31}' \cdot (k_{43}/k_{34}) = k_{31}'/K_{34} \qquad (16)$$

By using the previously determined values[21b] $k_{10} = (k_D [H_2O]) = 8.85 \times 10^{-4}$ *M*/sec., $k_{01} = 1.3 \times 10^{11} \, M^{-1}$ sec.$^{-1}$ and substituting experimental

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(21) (a) Σc_i^2 represents the bracket term in (12b). (b) M. Eigen and L. De Maeyer, *Z. Elektrochem.*, **59**, 986 (1955).

quantities, $(H^+) \approx 10^{-2}\ M$ and $(Cl_2) \approx 10^{-3}\ M$ we obtain

$$k_{13}' = k_{13} + \frac{k_{10}/(Cl_2)}{1 + \frac{k_{01}(H^+)}{k_{03}(Cl_2)}} = k_{13} + \frac{0.89}{1 + \frac{1.2 \times 10^{12}}{k_{03}}} \quad (17)$$

Since k_{03} cannot exceed $10^{10}\ M^{-1}$ sec.$^{-1}$, pathway ① → ⓪ → ③ must be insignificant, and we have directly

$$k_{13} = 11.0 \text{ sec.}^{-1} \text{ and } k_{31}/K_{34} = 1.80 \times 10^4\ M^{-1} \text{ sec.}^{-1}$$

A knowledge of protolytic reactions[17] permits us to make some estimations. At $\mu = 0.1\ M$, $k_{31} \approx 10^{10}\ M^{-1}$ sec.$^{-1}$; thus $K_{34} = k_{34}/k_{43} = (Cl^-)ClOH)/(Cl_2OH^-) \approx 5 \times 10^5\ M$. We see that the stability is far to the side of ClOH. Rate constant k_{43} must be appreciably lower than that of a diffusion controlled reaction. From K_{34}, K_{H_2O} and K_{ClOH} we calculate $K_{03}^{-1} = \frac{(OH^-)(Cl_2)}{(Cl_2OH^-)} \approx 10^{-5}\ M$ (and $k_{03} \leq 5 \times 10^9\ M^{-1}$ sec.$^{-1}$ diffusion controlled, $k_{30} \leq 10^5$ sec.$^{-1}$). Thus the relative stability of Cl_2OH^- with respect to Cl_2 and OH^- is quite large, but Cl_2OH^- is unstable with respect to loss of Cl^-. We may compare to Cl_3^-

$$K_{Cl_3^-} = 0.18\ M^{-1};\ K_{34}^{-1} \sim 10^{-6}\ M^{-1};\ K_{03} \sim 10^5\ M^{-1}$$

(b) **Bromine.**—Figure 3 can be interpreted as in the chlorine case.

The results at 20° and $\mu = 0.1\ M$ are

$$\overrightarrow{k} = 110 \text{ sec.}^{-1}$$
$$\overleftarrow{k} = 1.60 \times 10^{10}\ M^{-2} \text{ sec.}^{-1}$$
$$K_{BrOH} = 6.9 \times 10^{-9}\ M^2$$

K_{BrOH} determined from $\overrightarrow{k}/\overleftarrow{k}$ is in good agreement with the thermodynamic literature value.[7] There is no pH-dependence of $\overleftarrow{k}$, and an ideal concentration dependence is clearly exhibited; so we conclude that

$$\overrightarrow{k} = k_{13}' = k_{13} + \frac{k_{01}/(Br_2)}{1 + \frac{k_{01}(H^+)}{k_{03}(Br_2)}} = k_{13} + \frac{0.89}{1 + \frac{2.5 \times 10^{10}}{k_{03}}} \quad (19)$$

where $(H^+) = 2 \times 10^{-4}\ M$, $(Br_2) = 1 \times 10^{-3}\ M$. Thus, $\overrightarrow{k} = k_{13} = 110$ sec.$^{-1}$ and $\overleftarrow{k} = k_{31}/K_{34} = 1.60 \times 10^{10}\ M^{-2}$ sec.$^{-1}$; pathway ① → ⓪ → ③ is of no importance.

We may now estimate as we did for chlorine. With $k_{31} \approx 1 \times 10^{10}\ M^{-1}$ sec.$^{-1}$ we have $K_{34} = \frac{(Br^-)(BrOH)}{(Br_2OH^-)} \approx 1$ and

$$K_{03}^{-1} = \frac{(OH^-)(Br_2)}{(Br_2OH^-)} \approx 1 \times 10^{-6}\ M;$$
$$(k_{03} \approx 10^{10}\ M^{-1} \text{ sec.}^{-1},\ k_{30} \approx 10^{-1} \text{ sec.}^{-1};$$
$$k_{34} < 10^9 \text{ to } 10^{10} \text{ sec.}^{-1},\ k_{43} < 10^9 \text{ to } 10^{10}\ M^{-1} \text{ sec.}^{-1})$$

Thus, as in the chlorine mechanism, OH^- is more tightly bound in Br_2OH^- than Br^-

$$K_{Br_3^-} = 17\ M^{-1};\ K_{34}^{-1} \sim 1\ M^{-1};\ K_{03} \sim 10^6\ M^{-1}$$

(c) **Iodine.**—Since $\overrightarrow{k}$ is so much smaller than $\overleftarrow{k}$ [(IOH)(H$^+$) + (IOH)(I$^-$) + (I$^-$)(H$^+$)] for iodine, no attempt is made to have an independent evaluation of the equilibrium constant from Fig. 4.

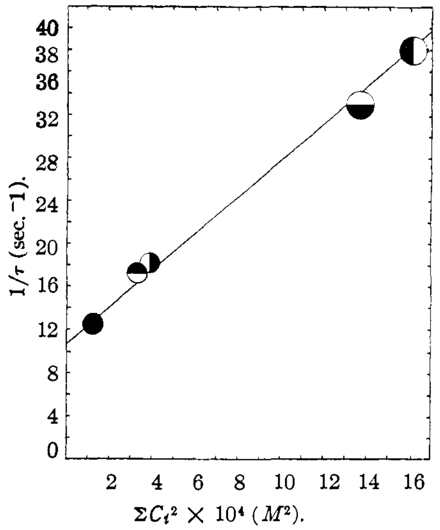

Fig. 2.—Concentration and pH dependence of the Cl_2 relaxation times (*cf.* 12b): ● $(Cl_2)_0 = 6.94 \times 10^{-3}\ M$, $(H^+) = 6.5 \times 10^{-3}\ M$; ◑ $(Cl_2)_0 = 1.3 \times 10^{-2}\ M$, $(H^+) = 1.1 \times 10^{-2}\ M$; ◐ $(Cl_2)_0 = 2.51 \times 10^2\ M$, $(H^+) = 8 \times 10^{-2}\ M$; ◓ $(Cl_2)_0 = 2.92 \times 10^{-2}\ M$, $(H^+) = 1.0 \times 10^{-2}\ M$; ◒ $(Cl_2)_0 = 3.76 \times 10^{-2}\ M$, $(H^+) = 2.1 \times 10^{-2}\ M$. (The upper two points include a somewhat greater error due to a reduction in effect size.)

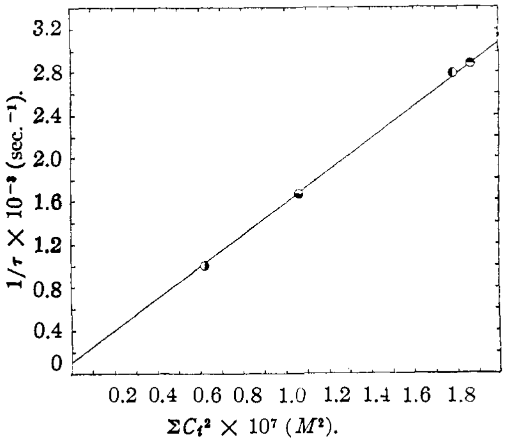

Fig. 3.—Concentration and pH dependence of the Br_2 relaxation times (*cf.* 12b): ◑ $(Br_2)_0 = 5.65 \times 10^{-4}\ M$, $(H^+) = 1.44 \times 10^{-4}\ M$; ◐ $(Br_2)_0 = 5.65 \times 10^{-4}\ M$, $(H^+) = 2 \times 10^{-3}\ M$; ◒ $(Br_2)_0 = 1.13 \times 10^{-3}\ M$, $(H^+) = 1.88 \times 10^{-4}\ M$; ◓ $(Br_2)_0 = 2.26 \times 10^{-3}\ M$, $(H^+) = 2.49 \times 10^{-4}\ M$.

The value for $\overleftarrow{k}$ is obtained from K_{IOH} through (11).

The over-all rate constants in this system at $T = 20°$ and $\mu = 0.1\ M$ are

$$\overrightarrow{k} = 3.0 \text{ sec.}^{-1}$$
$$\overleftarrow{k} = 4.4 \times 10^{12}\ M^{-2} \text{ sec.}^{-1}$$

From the observed concentration and pH dependency it follows that $k_{34} \gg k_{31}'(H^+)$ and therefore

$$\overrightarrow{k} = k_{13}' = k_{13} + \frac{k_{10}/(I_2)}{\frac{1 + k_{01}(H^+)}{k_{03}(I_2)}} = k_{13} + \frac{0.89}{1 + \frac{1.2 \times 10^9}{k_{03}}} \quad (20)$$

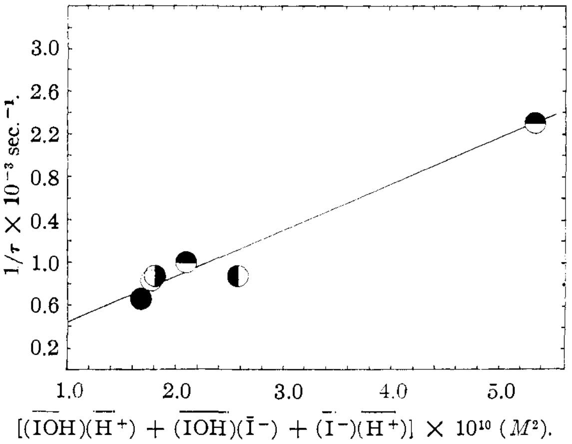

Fig. 4.—Concentration and *p*H dependence of the I_2 (*i.e.*, I_3^-) relaxation times (*cf.* 12b): ● $(I_2)_0 = 5.0 \times 10^{-4}$ *M*; $(H^+) = 1.0 \times 10^{-5}$ *M*; (upper) ◓ $(I_2)_0 = 1.0 \times 10^{-3}$ *M*; $(H^+) = 1.0 \times 10^{-4}$ *M*. In all other cases, $(I_2)_0 = 1.0 \times 10^{-3}$ *M*, and the measured value of (H^+) was equal or very close to 1.0×10^{-5} *M*.

We shall now examine $\overrightarrow{k}$, under substitution of the typical experimental conditions (*i.e.*, $(H^+) \approx 10^{-5}$ *M*, $\approx (I_2) = 10^{-3}$ *M*). It is probable that $k_{03} > 1.2 \times 10^9$ M^{-1} sec.$^{-1}$ ($k_{03} \approx 0.5$ to 1×10^{10} M^{-1} sec.$^{-1}$). From the results as demonstrated in Fig. 4 it follows that the value of k_{13} must be the difference between the measured term k_{13}' and the term $0.89/\left(1 + \frac{1.2 \times 10^9}{k_{03}}\right)$ whose smallest probable value is 0.89 sec. In any case, we may write with certainty: $k_{13} \geq 2.1$ sec.$^{-1}$, however ≤ 3 sec.$^{-1}$. Thus, we may conclude that for the unbuffered hydrolysis of the halogens the pathway ① → ⓪ → ③ is of significance only for iodine.

By comparing with our calculation of k_{13}', we see that k_{31}' must also be split into two terms corresponding to ① → ③ → ④ and ① → ⓪ → ③ → ④. We may begin with the part representing the direct reaction between iodine and molecular water. For this step, $k_{31}/K_{34} \approx 3.1 \times 10^{12}$ M^{-1} sec.$^{-1}$ (4.4×10^{12} M^{-2} sec.$^{-1}$ is the upper limit). From Connick and Chia (see Table I) $K_{34} = 3.34 \times 10^{-3}$ *M*, and therefore

$$k_{31} \approx 1.04 \times 10^{10}\ M^{-1}\ \text{sec.}^{-1} \text{ at } \mu = 0.1\ M, \text{ but}$$
$$k_{31} \approx 1.6 \times 10^{10}\ M^{-1}\ \text{sec.}^{-1} \text{ at } \mu = 0\ M$$

In this case a determination of k_{31} is directly possible, since the corresponding equilibrium constant was known from spectrophotometric and thermodynamic data. The value of k_{31} is consistent with the magnitude of rate constants of protolytic reactions which have been determined in great numbers. Considering the steric factor of the relatively bulky molecule-ion I_2OH^-, a value of about 2×10^{10} M^{-1} sec.$^{-1}$ is to be expected from theory.[17] Since the corresponding reactions of Br_2OH^- and Cl_2OH^- are of the same type, our above estimations for these species are plausible.

From the upper limit calculation, $k_{31}' = \overleftarrow{k} \cdot K_{34} = (4.4 \times 10^{12})(3.30 \times 10^{-3}) = 1.5 \times 10^{10}$ M^{-1} sec.$^{-1}$, it follows that $k_{34} \gg (k_{31}(H^+) = 1.5 \times 10^5$ sec.$^{-1}$) and $k_{43} \gg 5 \times 10^7$ M^{-1} sec.$^{-1}$. If we assume, as we have done throughout, a diffusion controlled value for k_{43}, we obtain $k_{43} \approx 5 \times 10^9$ M^{-1} sec.$^{-1}$, $k_{34} \approx 3 \times 10^7$ sec.$^{-1}$. Therefore the kinetic measurements lead to consistent upper and lower limits for the rate constants k_{34} and k_{43}. This calculation also constitutes a verification of the thermodynamic measurements of Connick and Chia. We may thus further calculate $K_{03}^{-1} = \frac{k_{30}}{k_{03}} = \frac{(I_2)(OH^-)}{(I_2OH^-)} = 6 \times 10^{-5}$ *M* from Table I (and estimate $k_{03} \approx 1 \times 10^{10}$ M^{-1} sec.$^{-1}$, $k_{30} \approx 6 \times 10^5$ sec.$^{-1}$). A comparison of the I_2OH^- equilibrium constants and the stability constant of I_3^- shows that for I_2OH^-, the OH^- is still bound tighter than I^- (but less than in the case of Br_2 and Cl_2)

$$K_{I_3} = 830\ M^{-1};\ K_{34}^{-1} = 3.0 \times 10^3\ M^{-1};\ K_{03} = 1.7 \times 10^4\ M^{-1}$$

Discussion

In Table II the measured over-all rate constants of halogen hydrolysis, valid for the conditions of the experiments (*i.e.* unbuffered halogen solution in the absence of additional acids or bases) are summarized. These data are certain within the given error limits of the experiments.

TABLE II

MEASURED OVER-ALL RATE CONSTANTS OF HALOGEN HYDROLYSIS

(Related to Mechanism I.) Temp = 293° *K*., μ = 0. 1 *M*

Rate constant	Cl_2	Br_2	I_2
$\overrightarrow{k}$ (sec.$^{-1}$)	11.0	110	3.0
$\overleftarrow{k}$ (M^{-2} sec.$^{-1}$)	$1.8_0 \times 10^4$	$1.6_0 \times 10^{10}$	$4.4_0 \times 10^{12}$

Furthermore, in Table III the rate constants of the individual steps are presented. The values in the first two rows follow directly from the experimental data. All other values are estimated and some of them may be safe only with respect to the orders of magnitude (*cf.* [a]). Nevertheless, the experiments strongly favor these estimations and allow us to draw some general conclusions.

The protolytic reactions (k_{31} and k_{03}) are throughout diffusion controlled (as directly measured for I_2), which is in agreement with our experience for many other similar systems. The formation rate of X_2OH^- from XOH and X^- can be diffusion controlled only as long as the stability of X_2OH^- with respect to XOH and X^- is high enough to favor this reaction. The corresponding rate constants are, nevertheless, smaller than k_{31} or k_{03}, the high values of which are due to the anomalous properties of excess and defect protons in aqueous solution. The dissociation rates (k_{13}, k_{30}, k_{34}) do not show a monotonic behavior.

This behavior is also reflected by the corresponding equilibrium constants which are represented in Table IV. Most of these values, again, are estimates which may be safe only with respect to the orders of magnitude. We shall examine these data for general trends amongst the three halogen congeners, providing a more detailed picture of their hydrolysis.

There are mainly two tendencies:

(a) The stability of "binary" compounds, such as X_2 or XOH decreases from Cl_2 to I_2, whereby

TABLE III

DETERMINED OR ESTIMATED RATE CONSTANTS OF INDIVIDUAL STEPS

(Related to Mechanism II) Temp. = 293°K.

Rate constant	Cl_2	Br_2	I_2	Remarks
k_{13} (sec.$^{-1}$)	11.0	110	2.1	Maximum at Br_2
$k_{31} \times \frac{k_{43}}{k_{34}}$ (M^{-2} sec.$^{-1}$)	$1.8_0 \times 10^4$	$1.6_0 \times 10^{10}$	3.1×10^{12}	Monotonic increase from Cl_2 to I_2
k_{31} (M^{-1} sec.$^{-1}$)	2×10^{10a}	2×10^{10a}	1.6×10^{10}	Diffusion controlled (measured for I_2)
k_{03} (M^{-1} sec.$^{-1}$)	10^{10a}	10^{10a}	10^{10a}	Diffusion controlled (for I_2 $k_{03} > 10^9$, measured)
k_{30} (sec.$^{-1}$)	2×10^{5a}	10^{4a}	6×10^{5a}	Minimum at Br_2
k_{34} (sec.$^{-1}$)		5×10^{9a}	3×10^{7a}	Decrease from Cl_2 to I_2
k_{43} (M^{-1} sec.$^{-1}$)	$\ll 5 \times 10^9$	5×10^{9a}	5×10^{9a}	Only for I_2 (and probably also for Br_2) diffusion controlled

[a] Estimated values.

TABLE IV

STABILITY CONSTANTS OF HALOGEN COMPOUNDS

	Cl_2	Br_2	I_2	Remarks
$K_{X_2} = \frac{(X_2^-)}{(X^+)(X^-)}$	$\sim 10^{30a}$	$\sim 10^{20a}$	$\sim 10^{11}$	Monotonic decrease (ref. 12)
$K_{04} = \frac{(XOH)(X^-)}{(X_2)(OH^-)}$	5×10^{10a}	10^{5a}	50	Monotonic decrease
$K_{X_3^-} = \frac{(X_3^-)}{(X_2)(X^-)}$	0.18	17	830	Monotonic increase
$K_{34}^{-1} = \frac{(X_2OH^-)}{(XOH)(X^-)}$	2×10^{-6a}	1^a	3×10^2	Monotonic increase
$K_{03} = \frac{(X_2OH^-)}{(X_2)(OH^-)}$	10^{5a}	10^{6a}	1.5×10^4	Maximum at Br_2

[a] Estimated values.

the relative stability of XOH is favored with respect to that of X_2 in the same order. This behavior is expressed by the equilibrium constants K_{X_2} and K_{04}, for which

$$K_{Cl_2} > K_{Br_2} > K_{I_2}$$

holds.

(b) The tendency of forming a "ternary" compound, such as X_3^- or X_2OH^- increases in the order $Cl_2 < Br_2 < I_2$. This behavior is expressed by the equilibrium constants $K_{X_3^-}$ and K_{34}^{-1} which express the relative stability of X_3^- or X_2OH^- with respect to X^- and X_2 or XOH.

At a first glance it seems as though K_{03} should belong to the latter category. However, for this equilibrium constant both tendencies (a and b) are present, acting in opposite directions. In other words, the tendency to form the "ternary" compound X_2OH^- *increases* from chlorine to iodine (*cf.* K_{34}^{-1}), but the relative stability of the hydroxo-compound—as expressed by K_{04}—*decreases* in the same order. Therefore it is plausible that K_{03} shows a maximum for bromine.

These trends are most directly exhibited by the rate constants. The k_{31} and k_{30} values show extrema at Br_2 since they are related to the relative stability of X_2OH^- with respect to X_2 and OH^- (*cf.* also the directly measured *k*-values). All other rate constants reflect the monotonic behavior to be expected from their physical and chemical properties.

The over-all mechanism of halogen hydrolysis is somewhat more complicated than for the previously studied cases of simple acids and bases (*cf.* tables in ref. 18.). This fact is a result of the nature of the symmetrical diatomic halogen molecule which necessitates the formation of an expanded-octet intermediate. The general mechanism (II) accounts for the entire range of possible conditions in the pure system (catalysis excepted), despite the fact that the data have been obtained from measurements in a restricted *p*H and concentration range. It should be emphasized that the steady state assumptions may fail in certain cases, whereupon the over-all expressions will assume different forms (*e.g.* direct reaction with OH^- at higher *p*H, etc.). However, since it was possible to determine or estimate nearly all the individual rate constants, one may well be able to formulate the over-all rate for any other condition.

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