



HOKKAIDO UNIVERSITY

Title	THE MECHANISM OF THE BASIC HYDROLYSIS AND THE BASE-CATALYZED CHLORIDE EXCHANGE OF CHLOROFORM
Author(s)	HINE, Jack
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 6(3), 202-206
Issue Date	1958-12
Doc URL	https://hdl.handle.net/2115/24682
Type	departmental bulletin paper
File Information	6(3)_P202-206.pdf



THE MECHANISM OF THE BASIC HYDROLYSIS AND THE BASE-CATALYZED CHLORIDE EXCHANGE OF CHLOROFORM

By

Jack HINE^{*)}

(Received December 26, 1958)

HORIUTI and KATAYAMA have recently described experiments on the effect of the concentration of alkali and of certain salts on the rates of the hydrolysis and the base-catalyzed radioactive chloride exchange of chloroform.¹⁾ They report three findings at variance with the mechanism for the basic hydrolysis of chloroform reported several years ago from this laboratory.²⁾ They report that the addition of NaCl and NaI does not cause V_d , the rate of chloroform hydrolysis, to decrease appreciably at a given hydroxide ion concentration, as demanded by the mechanism of HINE and DOWELL (HD). They also report that u_s , the rate of chloride exchange, is decreased somewhat by the addition of chloride or iodide at constant base concentration, but not nearly so much as demanded by the HD mechanism. Thirdly, they state that the ratio, u_s/V_d , does not decrease significantly with increasing base concentration as demanded by the HD mechanism.

It is the purpose of the present paper to comment on these three points, starting with the latter. From equations (10. V) and (10. u) of HORIUTI and KATAYAMA the ratio, V_d/u_s , can be seen to be interpreted on the basis of the HD mechanism as

$$\frac{V_d}{u_s} = \frac{k_w[\text{H}_2\text{O}] + k_h[\text{OH}^-]}{k_{\text{Cl}}} = \frac{[\text{H}_2\text{O}]}{k_{\text{Cl}}/k_w} + \frac{(k_h/k_w)[\text{OH}^-]}{k_{\text{Cl}}/k_w}$$

Thus the HD mechanism predicts that in the absence of added salts a plot of V_d/u_s versus $[\text{OH}^-]$ should give a straight line of slope $(k_h/k_w)/(k_{\text{Cl}}/k_w)$ and intercept $[\text{H}_2\text{O}]/(k_{\text{Cl}}/k_w)$. The HTT mechanism predicts that this plot should be a straight line of zero slope and does not predict

*) School of Chemistry, Georgia Institute of Technology, Atlanta, U.S.A.

1) J. HORIUTI and M. KATAYAMA, this Journal **6**, 57 (1958).

2) J. HINE and A. M. DOWELL, Jr., J. Am. Chem. Soc. **76**, 2688 (1954).

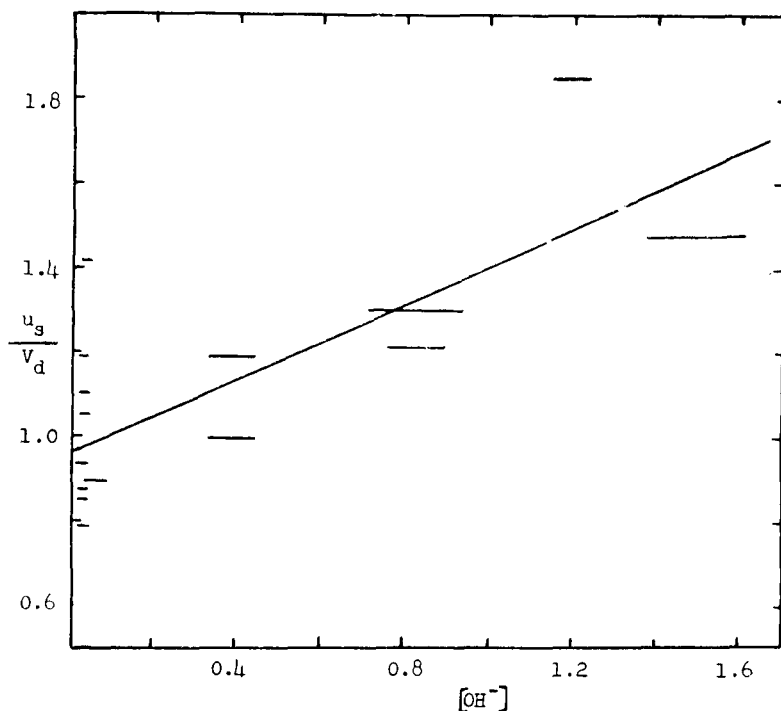


Fig. 1. Plot of u_s/V_d versus $[\text{OH}^-]$.

the intercept. The plot of the experimental data shown in Fig. 1 contains points deviating considerably from any straight line, but it seems clear that the best straight line through the points has a slope significantly larger than zero. The intercept is seen to be about 0.96 in quite satisfactory agreement with the value 0.90 ± 0.14 that may be calculated from the published values of k_{c1}/k_w .²⁾ Unfortunately, as previously stated²⁾ "we have not made kinetic studies...to permit a determination of k_h/k_w ." From the slope of the line in Fig. 1 (about 0.44) a k_h/k_w value of about 27 may be calculated. Although this value may be in error by as much as 30-40% because of various experimental uncertainties, it is clearly smaller than the value 229, calculated previously on the basis of the equation of SWAIN and SCOTT.³⁾ It therefore seems clear that the equation of SWAIN and SCOTT deviates considerably from the experimental data in the present case, although no more

3) C. G. SWAIN and C. B. SCOTT, J. Am. Chem. Soc. **75**, 141 (1953).

than it does in certain other recorded cases.

With regard to V_a , the rate of hydrolysis, it would appear that in the presence of large concentrations of base that do not change greatly during the reaction, the most reliable determinations are those based on chloride ion analysis. In runs like 22, 23 and 25, carried out in the presence of considerable concentrations of chloride or iodide ions, the reaction should be capable of being followed better by measurements of the base concentrations. For example, if, in run 23, the initial determination of chloride ion concentration gives a value 1% larger than that actually present and the final determination gives a value 1% below the true value, then the value of $\Delta[\text{Cl}^-]$ determined will be about three times as large as the actual value. Analogous errors in hydroxide ion determinations, however, would produce only a 3.5% error in $\Delta[\text{OH}^-]$. Therefore the effect of added salts on the rates of chloroform hydrolysis as shown by the measurements of HORIUTI and KATAYAMA on changes in the base concentration will be considered here. Since the chloroform concentration is held constant by the presence of an excess of a separate chloroform phase, the reaction may be treated as a (pseudo) first order disappearance of hydroxide ions. The rate constant for the process is defined by the equation

$$k = \frac{2,303}{t} \log \frac{[\text{OH}^-]_0}{[\text{OH}^-]_t}$$

TABLE I. Hydrolysis Rates in the Presence of Added Salts.

Run No.	Added Salt (M)	$10^4 k$ (min^{-1})	$10^6 u_s$
20	none	16.8	11.2
21	none	16.2	12.0
22	0.571 NaCl	11.0	8.6
23	0.969 NaCl	6.7	4.4
24	1.003 NaClO ₄	13.1	11.5
25	0.469 NaI	3.8	4.5
26	0.424 NaF	14.3	10.9
27	0.841 NaOAc	15.3	8.4
28	1.177 Na ₂ SO ₄	13.0	12.1

Values of k calculated from the data of HORIUTI and KATAYAMA's runs 20 through 28 are listed in Table I. From the equations derived

earlier²⁾ and values of k_{Cl}/k_w ⁴⁾ the HD mechanism predicts that 0.571 M sodium chloride should decrease the hydrolysis rate to 62%, and 0.969 M sodium chloride to 48% of its value in the absence of chloride. In the absence of ionic strength effects this would lead to predictions of k values of 10.2 and 7.9 in runs 22 and 23. Since there seems to be a definite, although small, negative ionic strength effect, these estimates should perhaps be reduced somewhat further but their agreement with the experimental values is still believed to be satisfactory.

The prediction of the effect of iodide ion at any finite time is more complicated, since in the presence of iodide ion dichloriodomethane is formed and subsequently it may hydrolyze. Application of the equations^{2,4)} used previously shows that 0.469 M sodium iodide should reduce the rate to 20% at the beginning of the reaction but that this value should increase (although by no more than 5%) as the reaction proceeds.⁵⁾ The prediction of a k value of 3.4 therefore seems in reasonable agreement with the data on run 25.

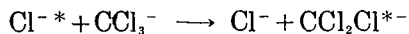
From the HD mechanism it may be seen that added halide ions will decrease the fraction of dichloromethylene molecules that react with radiochloride ions by exactly the same factor as they decrease the fraction that react with water. Therefore added halide ions will have the same effect on the chloride exchange rate as on the hydrolysis rate (neglecting ionic strength effects). Hence we would expect the radioactivity of the chloroform to be proportional to the change in hydroxide ion concentration in a given run. Taking runs 20 and 21 as reference runs, in which 83.5 ± 1.5 counts per minute accompanied a change of 0.03635 ± 0.00025 M in the base concentration, we might expect in runs 22, 23 and 25 where 0.0300 M, 0.0220 M and 0.0143 M base were used up to get activities of 69, 51 and 33 counts per minute.⁶⁾ These values compare with the experimental values of 66, 35 and 33, the only significant difference being in run 23, where chloride ions had a *greater* effect than predicted by the HD mechanism. In this connection it might be mentioned that while the HTT mechanism, attribu-

4) Since the work of HORIUTI and KATAYAMA permits a *determination* of k_h/k_w as about 27, this value should replace the earlier *estimate* (229). This change will decrease all of the k_c/k_w values given previously by 5-10%. In the present calculations we have used an average k_{Cl}/k_w value of 60 and a k_I/k_w value of 470.

5) Note that k_I/k_w had to be determined by the extrapolation of climbing rate constants to zero time (Ref. 2).

6) The last value could be as much as 5% higher due to subsequent reaction of dichloriodomethane.

ting exchanged to the reaction



predicts *no* effect of added halide ions on the exchange rate at constant ionic strength, it predicts a large *increase* in exchange with increasing ionic strength (since the reaction is between two ions of like charge). No evidence for such an increase appears to have been found, however.

While there is no clear evidence from the work of HORIUTI and KATAYAMA that perchlorate, fluoride or sulfate ions react with dichloromethylene, it does seem very likely that acetate ions do and that this is responsible for the decrease in the exchange rate in run 27. There is no effect on the observed hydrolysis rate in this run because the compound $\text{CH}_3\text{CO}_2\text{CHCl}_2$ formed by the CCl_2 capture should be hydrolyzed quite rapidly under the reaction conditions.

Summary

It is believed that the data on the effect of added salts on the rates of chloroform's hydrolysis and radioactive chloride exchange and the effect of added base on the ratio V_a/u_s all give new experimental support to the HD mechanism.

The author is indebted to Dr. K. TANABE and Mr. M. KATAYAMA for discussions of this subject and to Prof. J. HORIUTI for the opportunity to express his views in the same volume of this journal as the paper of HORIUTI and KATAYAMA.