ANOMALOUS SALT EFFECT ON THE RATE OF HYDROLYSIS OF CHLOROFORM

By

Kozo TANABE and Yoshihisa WATANABE*)

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Introduction

We have studied the effect of pH on the rate of hydrolysis of chloroform and reported an unusual pH-rate profile involving a rate maximum near pH 4[1]. Recently HINE and LANGFORD have reinvestigated the pH effect and found no evidence for the reported maximum[2]. The existence of the rate maximum can be interpreted neither by the mechanism in acidic solution nor by that in alkaline solution which were reported by HINE and his co-workers[2][3], while our mechanism has been deduced from the rate maximum[1]. They suggested that in basic solution chloroform hydrolyses *via* the intermediates trichloromethyl anion and dichloromethylene, and in acidic solution there is a first-order solvolysis that is largely S_N2**) in character. On the other hand, our mechanism involves an isomer of chloroform besides their intermediates, dichloromethylene being formed by an entirely different process from theirs. These differences between both of the mechanisms are based essentially on the difference of the experimental data on the rate of hydrolysis around pH 4. Most of our runs were now conducted at ionic strength of 10^{-3}~10^{-6}, whereas in buffer solutions at ionic strength of 0.2 in their case, which might have made the difference. Therefore in the present work we have investigated carefully the salt effect on the rate of hydrolysis of chloroform in acidic region in question.

It has been found that the rate maximum lowered and shifted toward higher pH with the increasing salt concentration and at last disappeared on the addition of 0.2 N sodium sulfate, although the rate maximum at pH 4 has been reproduced in the absence of any added salts. The above experimental results involve a pronounced salt effect on the rate *e.g.*, that 0.01N or 0.2 N Na_2SO_4 decreases the rate by about six-fold or sixteen-fold at least respectively,

*) K. T.: Research Institute for Catalysis, Hokkaido University.
Y. W.: Department of Chemistry, Faculty of Science, Hokkaido University, now at Nippon Electric Co. Kawasaki.

**) For the meaning of the term S_N2, see J. HINE, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, N. Y., 1956, Chap. 5.

which indicates that the salt effect on the appropriate activated complex must be appreciable. In the light of the observed salt effect, the mechanism of hydrolysis of chloroform is discussed.

Results and Discussion

Table 1 shows the results of the hydrolysis of chloroform followed by pH meter either with or without addition of salt respectively. Each series in the Table includeds several parallel runs initiated with the same quantities of chloroform, aqueous solution and added reagents shown respectively in the

TABLE 1. Hydrolysis of chloroform in aqueous solution at 100°C followed by pH meter.

Series	Quantity of chloroform cc at room temp.	Quantity of aqueous solution cc at room temp.	Additions	Time of contact (min.)	pH at room temp.	pH at 100°C	Room temp. °C
1	1	5	None	0	5.35	5.78	20
	"	"		10	5.60	5.59	"
	"	"		20	5.22	5.22	"
	"	"		30	4.72	4.72	"
	"	"		40	4.08	4.08	"
	"	"		65	3.60	3.60	"
	"	"		110	3.35	3.35	"
2	1	5	Ca. 10^{-4}N-H_2SO_4 *)	0	4.20	4.20	20
	"	"		10	3.80	3.80	"
	"	"		20	3.70	3.70	"
	"	"		40	3.56	3.56	"
	"	"		60	3.42	3.42	"
	"	"		100	3.36	3.36	"
	"	"		270	3.16	3.16	"
3	1	5	0.01 N-Na_2SO_4	0	5.86	5.80	20
	"	"		10	5.55	5.55	"
	"	"		23	4.88	4.90	"
	"	"		32	4.33	4.36	"
	"	"		50	4.04	4.07	"
	"	"		100	3.75	3.78	"
4	1	5	0.2 N-Na_2SO_4	0	6.32	6.03	20
	"	"		10	5.10	5.15	"
	"	"		25	4.55	4.60	"
	"	"		40	4.35	4.40	"
	"	"		90	3.75	3.80	"
5	1	5	0.2 N-Na_2SO_4	0	5.90	5.84	20
	"	"		10	5.05	5.10	"
	"	"		25	4.58	4.63	"
	"	"		40	4.20	4.25	"
	"	"		65	4.10	4.15	"
	"	"		120	3.71	3.76	"

*) This was added to make the pH of the initial solution 4.20.

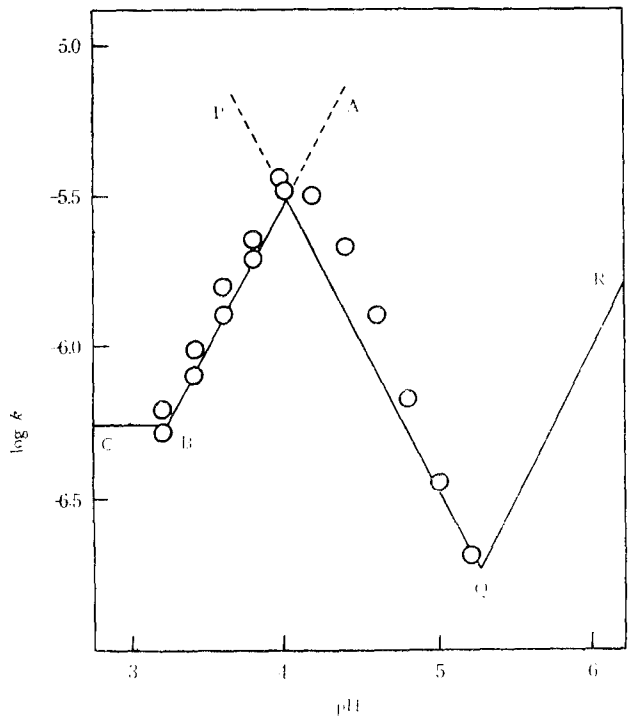

Fig. 1. Hydrolysis of chloroform in the absence of added salt. Solid lines show the previous data.

second to the fourth column, but of different time of contact shown in the fifth column, where zero of time in particular corresponds to the initial condition. All runs were conducted at 100 C.

Next columns give pH measured at room temperature and pH at 100 C calculated according to the previous method[1]. The rates of hydrolysis shown in Fig. 1 to 3 were calculated from the data of Table 1 as described later.

The results with no added salt have reproduced the rate maximum near pH 4 which was obtained previously as shown in Fig. 1, where log k was plotted against pH. In this case the concentration of salt which was formed due to the decomposition of chloroform is estimated to be about 10^{-3}N at most. Since chloroform distilled in nitrogen was used this time, it seems impossible that the reaction of a small amount of some reactive impurity such as phosgene in the chloroform may account for the observed data, as HINE and LANGFORD pointed out[2]. The addition of 0.01 N sodium sulfate, however, caused the pH-rate profile to change strikingly as shown in Fig. 2. It has been found on the addition of 0.2 N sodium sulfate that the rate maximum does disappear

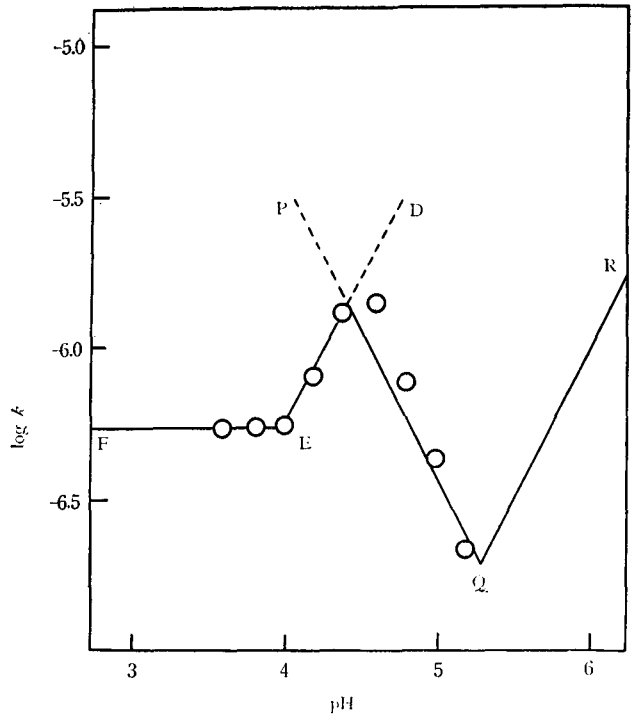

Fig. 2. Hydrolysis of chloroform in the presence of 0.01 N sodium sulfate.

as shown in Fig. 3. That was the case observed by HINE and LANGFORD who conducted most of the runs in buffer solutions at ionic strength of 0.2[2].

The striking results that 0.01 N salt decreased the rate by about six-fold and 0.2 N salt by sixteen-fold at least cannot be accounted for by the well known neutral salt effect dealt with by Brönsted. The fact would require that the salt effect on the appropriate activated complex must be appreciable.

The rate maximums shown in Fig. 1 and 2 cannot be interpreted by the mechanisms of hydrolysis presented by HINE and *et al.*[2][3] According to their mechanisms, pH has no effect on the rate of hydrolysis in acidic solution, while the rate increases proportionally with increasing pH in alkaline solution.

It was previously described in detail that our mechanism has been deduced from the rate maximum at pH 4 shown in Fig. 1[1]. That the rate maximum dies away as shown in Figs. 2 and 3 may be attributed in accordance with our mechanism to the pronounced salt effect on the rate as follows. ABC of Fig. 1 represents the second elementary step of our mechanism which controlls the hydrolysis in acidic region[1],

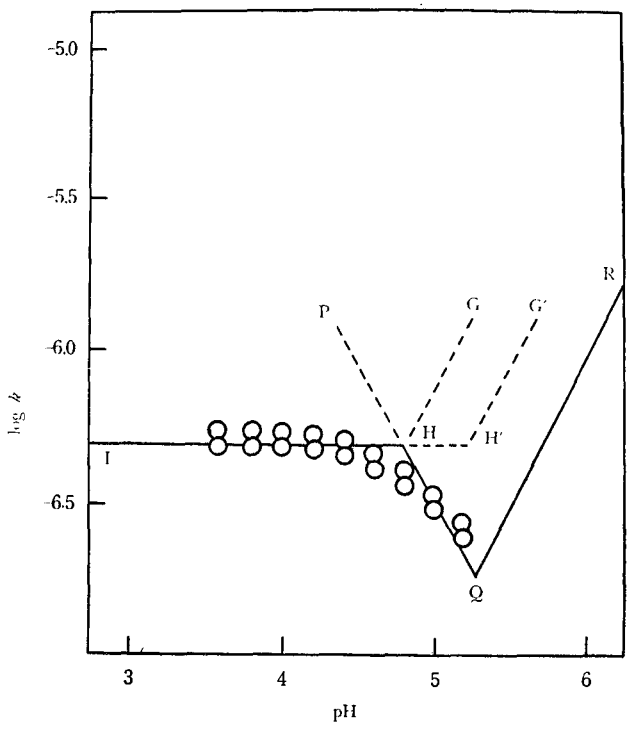

Fig. 3. Hydrolysis of chloroform in the presence of 0.2 N sodium sulfate.

$$CCl_3^- + HA \longrightarrow CCl_2{}^{\times}_{\times}ClH + A^- \qquad (2)$$

preceded by the first elementary step which is in equilibrium,

$$CHCl_3 + B \longrightarrow CCl_3^- + H^+B \qquad (1)$$

where HA and B denote Brönsted acid and base respectively and $CCl_2{}^{\times}_{\times}ClH$ an isomer of chloroform. The step (2) where HA is H_2O or H_3O^+ is responsible for the part AB or BC respectively*). The third step which controlls the hydrolysis in alkaline solution,

$$B + CCl_3{}^{\times}_{\times}ClH + HA \longrightarrow BH^+ + CCl_2 + ClH + A^- \qquad (3)$$

is expressed by PQR in the Figures. The part PQ is the particular case of step (3) when HA and B are H_3O^+ and H_2O respectively.

The Figures show that the parts BC and PQ are not changed much by the addition of sodium sulfate. It is the part AB that changed strikingly, *e.g.*,

*) Cf. p. 181 of Ref. 1.

0.01 N salt changed the part AB into DE of Fig. 2 and 0.2 N salt changed the part AB into GH or G'H' of Fig. 3 which are entirely concealed because the part PQ is the rate controlling step in the pH region.

Thus the results of Figs. 2 and 3 are accounted for by assuming an outstanding salt effect on the activated complex of step (2) in the case when HA is H_2O.

Experimental

One cc of chloroform was shaken briskly in the absence of air with 5 cc of aqueous solution of known pH either with or without addition of salt at 100°C for a recorded time in a quartz tube of 18～25 cc capacity, the quartz tube was opened, several cc of the solution pippetted out and the pH was determined at room temperature similarly as described previously[1].

The experiment in the absence of air was carried out by freezing preliminarily the content of the reaction tube by liquid nitrogen, evacuating the latter 10^{-5}～10^{-6} mmHg, allowing it to melt in order to give off the occuluded air, the tube being shut off from the vacuum line in the mean time, and then by repeating the above procedure several times similarly as in the previous work[1)4)].

Purchased chloroform of reagent grade was washed with conc. sulfuric acid and distilled water and then distilled in nitrogen which was passed bubbling through alkaline solution of pyrogallol in order to remove trace of oxygen.

Calculation of rate constants

Rate constants were calculated from the change of pH shown in Table 1 as follows. Admitting that a chloroform molecule, as it decomposes, yields three chloride ions, the rate of hydrolysis k reckoned to unit volume of solution is expressed as,

$$k = \frac{1}{3} \cdot \frac{d\Delta[Cl^-]}{dt} \qquad (4)$$

where $\Delta[Cl^-]$ is the increment of chloride ion concentration $[Cl^-]$ in solution due to decomposition and t the time of contact.

Neglecting the formate evolution by decomposition*), we have, because of electric neutrality of the solution,

$$2[SO_4^=] + \Delta[Cl^-] + [OH^-] = [H^+] + [Na^+] \qquad (5)$$

where $[SO_4^=]$ and $[OH^-]$ *etc.* are normal concentrations of sulfate ion and hydroxide ion *etc.*

Substituting Eq. (5) for Eq. (4), we obtain,

*) The validity of the neglect is shown in Table 7, p. 161 of Ref. 1.

$$k = \frac{1}{3}\left(\frac{d[H^+]}{dt} + \frac{d[Na^+]}{dt} - \frac{d[OH^-]}{dt} - 2\frac{d[SO_4^{=}]}{dt}\right). \qquad (6)$$

Since $[Na^+]$ and $[SO_4^{=}]$ are kept constant in this case, $d[Na^+]/dt$ and $d[SO_4^{=}]/dt$ become zero. Rewriting $[OH^-]$ or $[H^+]$ into respective ratio of activity a^{OH} or a^{H^+} to the activity coefficient f^{OH^-} or f^{H^+} and introducing the thermodynamical dissociation constant,

$$K_h = a^{H^+}a^{OH^-} \qquad (7)$$

we have,

$$k = \frac{1}{3}\left(\frac{da^{H^+}/f^{H^+}}{dt} - \frac{dK_h/a^{H^+}f^{OH^-}}{dt}\right). \qquad (8)$$

This, upon differentiation, yields

$$k = \frac{1}{3}\left\{\frac{f^{H^+}\frac{da^{H^+}}{dt} - a^{H^+}\frac{df^{H^+}}{dt}}{(f^{H^+})^2} + \frac{\left(f^{OH^-}\frac{da^{H^+}}{dt} + a^{H^+}\frac{df^{OH^-}}{dt}\right)K_h}{(a^{H^+}f^{OH^-})^2}\right\}. \qquad (9)$$

Rearranging, we have

$$k = \frac{1}{3}\cdot\frac{d\log a^{H^+}}{d\log t}\cdot\frac{a^{H^+}}{t}\times \left\{\frac{K_h}{(a^{H^+})^2 f^{H^+}}\left(1 + \frac{d\log f^{H^+}}{d\log a^{H^+}}\right) + \frac{1}{f^{H^+}}\left(1 - \frac{d\log f^{H^+}}{d\log a^{H^+}}\right)\right\}. \qquad (10)$$

The logarithmic form of Eq. (10) is given by

$$\log k = -0.477 + \log\frac{d\log a^{H^+}}{d\log t} + \mathrm{pH} - \log t + \log\left\{\frac{K_h}{(a^{H^+})^2 f^{H^+}}\left(1 + \frac{d\log f^{H^+}}{d\log a^{H^+}}\right) + \frac{1}{f^{H^+}}\left(1 - \frac{d\log f^{H^+}}{d\log a^{H^+}}\right)\right\} \qquad (11)$$

f^{H^+} and f^{OH^-} are calculated similarly as described previously[1]. $\frac{d\log a^{H^+}}{d\log t}$ is obtained from tangent of pH *vs.* log t curves at desired pH. Rate constants calculated by Eq. (11) are in good agreement with the values calculated by the different equation derived previously*).

*) Cf. pp. 148~151 of Ref. 1.

Acknowledgments

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