THE VELOCITY OF SPLITTING OFF OF CHLORINE FROM MONOCHLORACETATE.

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When monochloracetic acid is acted on by water, it is partially converted into glycolic acid and hydrochloric acid, according to the equation

$$CH_2ClCOOH+H_2O = CH_2OHCOOH+HCl.$$

The velocity of this decomposition or hydrolysis is very slow, but that of the salt is rapid and especially accelerated by the presence of alkalies in excess.

Many investigations on this subject have been carried out. Buchanan(1) made a study of the velocity of decomposition by heating the solution of monochloracetate. Lossen and Eihoff(2) measured the velocity of decomposition at room temperature. After keeping the solution for 500 days, the quantity of decomposed product was determined. Euler(3) repeated Schwab's(4) experiment on the velocity of decomposition of monochloracetate by the presence of sodium hydroxide at 65 and 80°C. Senter(5) investigated the velocities of decomposition of monochloracetic acid and its salts, with or without caustic soda at 74.4 and 102°C. Johanson(6) measured the velocity of reaction of the barium salt with barium hydroxide, and of the sodium salt with sodium hydroxide respectively at 250°C. But their concentration of the solution was determined after a long interval from the start of reaction. Drushel and Simpson(7) also measured the velocity of decomposition of sodium monochloracetate at 70 and 90°C. Euler and Fahlander(8) investigated the velocity of decomposition of sodium monochloracetate with sodium hydroxide or with other catalysers. Hedelius(9) determined the velocity of splitting off of chlorine from monochloracetate, acting with sodium hydroxide at 55–90°C.

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(1) *Ber.*, **4** (1971), 340, 863.
(2) *Ann.*, **342** (1905), 116.
(3) *Ber.*, **39** (1906), 2726.
(4) *Etades Dyn. chem.* 1884, 20.
(5) *Z. physik. Chem.*, **70** (1910), 511.
(6) *Z. physik. Chem.*, **79** (1912), 621.
(7) *J. Am. Chem. Soc.*, **39** (1917), 2456.
(8) *Z. physik. Chem.*, **100** (1922), 171.
(9) *Z. physik. Chem.*, **96** (1920), 343.

Thus many papers are published on this subject, yet in none of them can be found the determination of the course of reaction in earlier stage at lower temperature.

The author has made a research on the velocity of the reaction within about 3 hours with or without caustic alkali at 25–35°C. The results obtained are reported below.

Theoretical.

As above mentioned, monochloracetate is decomposed in aqueous solution with caustic alkali as the following:—

$$CH_2ClCOOK + KOH = CH_2OHCOOK + KCl$$

Assuming that a represents the initial concentration (in mols) of monochloracetate, b that of caustic alkali and x the decomposed amount of monochloracetate (or produced chloride) at the end of time t, the velocity of the reaction can be expressed by

$$\frac{dx}{dt} = k(a-x)(b-x) \; ,$$

k being the constant of velocity.

In case $a \neq b$, on integration, we obtain the expression

$$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = kt \; ,$$

or

$$e^{(a-b)kt} = \frac{b(a-x)}{a(b-x)} \; .$$

As x and kt are small and the high powers of $\frac{x}{a}$ and $\frac{x}{b}$ can be neglected, we may write

$$1+(a-b)kt = \left(1-\frac{x}{a}\right)\left(1+\frac{x}{b}\right) .$$

then

$$1+(a-b)kt = 1-\frac{x}{a}+\frac{x}{b} \; .$$

Hence

$$k = \frac{x}{abt}$$

In case $a = b$, the equation becomes

$$\frac{dx}{dt} = k(a-x)^2 ,$$

which gives, on integration,

$$\frac{1}{a-x} - \frac{1}{a} = kt ,$$

or

$$\frac{x}{a\ a-x)} = kt .$$

As x is small, we may write

$$k = \frac{x}{a^2 t} .$$

In either case, the decomposed quantity of monochloracetate (or produced chloride) is proportional to the product of concentrations of both monochloracetate and caustic alkali at their initial state and the time. If monochloracetate has been decomposed partially at initial state, we must write $x = \alpha + \beta t$ instead of $x = kabt$, where α represents the decomposed monochloracetate at initial state and $\beta = k.a\,b$.

In the case where only monochloracetate exists in the solution, the reaction may be as follows:—

$$CH_2ClCOOK + H_2O = CH_2OHCOOH + KCl.$$

As the reaction proceeds, the acidity of the solution increases. This reaction to some extent may be considered as monomolecular. Hence the velocity of the reaction can be expressed as follows:—

$$\frac{dx}{dt} = k(a-x)$$

where a is the concentration of monochloracetate at initial state, and x the decomposed quantity of this salt at time t. On integration, we have

$$\ln \frac{a}{a-x} = kt .$$

As x and kt are small, we may write

$$k = \frac{x}{at} .$$

Similarly as described above, in case monochloracetate has been decomposed partially at first, we may write $x = \alpha + \beta t$ instead of $x = kat$, where $\beta = ka$.

If we measure the concentration of produced chloride and the time, we can calculate the velocity constant of the reaction.

Experimental.

The experiment is carried out as follows. The solutions of monochloracetic acid and caustic alkali are kept in a thermostat, and mixing the two solutions, a portion of the solution is drawn out at a certain time and a silver nitrate solution is added both to this sample acidified with nitric acid and to the standard solution of potassium chloride. The two solutions are compared by using the nephelometer of Clet Co.

The chemicals used are obtained from Kahlbaum. The results of the experiments are shown in Tables 1, 2 and 3.

Table 1.

$CH_2ClCOOK + KOH$

Exp. No.	Temp. C.	Initial state (M.)	$\beta \times 10^4$	t. min.	$x \times 10^4$(M.) obs.	$x \times 10^4$(M.) calc.
1	20	$a = 0.3113$ $b = 0.2965$	0.02092	30	3.30	3.24
				60	3.82	3.87
				91	4.45	4.51
				125	4.94	5.23
				150	5.95	5.75
				180	6.61	6.38
				210	7.05	7.00
				240	7.53	7.63
				270	8.19	8.26
2	25	$a = 0.3000$ $b = 0.3000$	0.04195	20	2.68	2.51
				40	3.42	3.35
				60	3.89	4.19
				90	5.30	5.45
				150	8.08	7.96
				180	9.59	9.22
				210	10.20	10.48
3	25	$a = 0.3084$ $b = 0.4077$	0.07230	30	4.61	4.43
				60	6.85	6.60
				90	8.35	8.77
				120	10.65	10.94
				150	13.02	13.10
				180	15.63	15.27

Table 1.—(*Concluded*)

Exp. No.	Temp. C.	Initial state (M.)	$\beta \times 10^4$	t. min.	$x \times 10^4$(M.) obs.	$x \times 10^4$(M.) calc.
4	30	$a = 0.3000$ $b = 0.3000$	0.12117	40	4.54	3.79
				60	6.85	6.22
				90	8.46	9.85
				120	13.04	13.49
				150	17.44	17.12
				180	19.63	20.76
				210	25.66	24.39
5	30	$a = 0.4000$ $b = 0.3000$	0.13593	30	4.50	4.20
				45	6.16	6.24
				60	7.37	8.28
				90	12.73	12.36
				120	16.69	16.44
				150	19.24	20.52
				180	28.15	24.59
				210	26.47	28.67
6	30	$a = 0.4000$ $b = 0.4000$	0.20095	40	7.76	5.84
				60	10.00	9.85
				90	15.31	15.88
				120	21.44	21.91
				150	22.52	27.94
				180	36.88	33.97
				210	41.48	40.00
7	30	$a = 0.5000$ $b = 0.5000$	0.29491	40	14.65	15.18
				60	21.62	21.08
				90	30.26	29.93
				120	38.43	38.77
8	30	$a = 0.3000$ $b = 0.3000$ $KNO_3 = 0.5000$	0.07226	12	2.73	2.72
				25	3.47	3.66
				40	4.85	4.74
				60	6.13	6.19
				90	8.47	8.35
				120	10.38	10.52
				150	13.35	12.69
				180	14.20	14.86
				210	17.16	17.02

Table 2.

$CH_2ClCOONa+NaOH$

Exp. No.	Temp. C.	Initial state (M.)	$\beta\times10^4$	t. min.	$x\times10^4$(M.) obs.	$x\times10^4$(M.) calc.
9	25	$a=0.3000$ $b=0.3000$	0.034472	10	1.08	1.07
				20	1.36	1.42
				40	2.07	2.11
				60	2.58	2.80
				90	3.87	3.83
				120	5.28	4.86
				150	5.93	5.90
				180	6.65	6.93
10	30	$a=0.3000$ $b=0.3000$	0.063324	30	2.59	2.23
				60	4.03	4.13
				90	6.09	6.03
				120	7.17	7.93
				180	12.19	11.73
11	35	$a=0.3000$ $b=0.3000$	0.19602	10	1.90	1.00
				30	4.72	4.92
				60	7.95	10.80
				90	18.32	16.68
				120	24.49	22.57
				150	27.05	28.45

Table 3.

$CH_2ClCOOK+H_2O$

Exp. No.	Temp. C.	Initial state (M.)	$\beta\times10^4$	t. min.	$x\times10^4$(M.) obs.	$x\times10^4$(M.) calc.
12	25	0.3000	0.002512	20	1.62	1.69
				60	1.84	1.80
				90	1.88	1.87
				120	2.02	1.95
				150	2.07	2.02
				180	2.00	2.10
				210	2.17	2.17
13	30	0.5000	0.01849	30	1.74	1.67
				45	1.86	1.95
				60	2.22	2.23
				80	2.63	2.60
14	30	0.5000	0.01361	10	1.64	1.56
				25	1.70	1.76
				40	1.86	1.96
				70	2.43	2.37

β is calculated by the method of least squares and then k is obtained from $\beta = kab$ or $\beta = ka$.

In experiment No. 8, beside the reacting substances, potassium nitrate was added; it is shown that the reaction velocity is retarded by the presence of another salt with a common ion.

Tables 4 and 5 give the resumes of the values at each temperature. The results of calculation show a fair agreement with the theory which we assumed at first.

Table 4.

Exp. No.	Temp. C.	Initial conc. (M)		$\beta \times 10^4$	$k \times 10^4$ mean	
		$CH_2ClCOOK$	KOH			
1	20	0.3113	0.2965	0.02092	0.227	
2	25	0.3000	0.3000	0.04195	0.466	0.521
3	,,	0.3084	0.4077	0.07230	0.575	
4	30	0.3000	0.3000	0.12117	1.35	1.23
5	,,	0.4000	0.4000	0.13593	1.13	
6	,,	0.4000	0.4000	0.20095	1.26	
7	,,	0.5000	0.5000	0.29491	1.18	
8	,,	0.3000	0.3000	0 07226		
			$KNO_3 = 0.5000$			
Exp. No.	Temp.	CH_2COONa	NaOH	$\beta \times 10^4$	$k \times 10^4$	
9	25	0.3000	0.3000	0.034472	0.381	
10	30	0.3000	0.3000	0.063324	0.704	
11	35	0.3000	0.3000	0.196020	2.18	

Table 5.

Exp. No.	Temp. C	Initial conc. (M.) $CH_2ClCOOK$	$\beta \times 10^4$	$k \times 10^6$ mean	
12	25	0 3000	0.002512	0.8372	
13	30	0.5000	0.01849	3.698	3.21
14	30	0.5000	0.01361	2.72	

In conclusion the author expresses his thanks to Mr. Sigeru Kondô for his assistance.

Summary.

1. Assumed as monomolecular reaction, the velocity of the decomposition of potassium monochloracetate in aqueous solutions is measured,

$$k_{25^\circ} = 0.837 \times 10^{-6} \text{ and } k_{30^\circ} = 3.21 \times 10^{-6}$$

2. The velocities of the following reactions are measured,

$$CH_2ClCOOK + KOH = CH_2OHCOOK + KCl$$

$$k_{20^\circ} = 0.227 \times 10^{-4},\ k_{25^\circ} = 0.521 \times 10^{-4} \text{ and } k_{20^\circ} = 1.23 \times 10^{-4}$$

$$CH_2ClCOONa + NaOH = CH_2OHCOONa + NaCl$$

$$k_{25^\circ} = 0.381 \times 10^{-4},\ k_{30^\circ} = 0.704 \times 10^{-4} \text{ and } k_{35^\circ} = 2.18 \times 10^{-4}$$

The velocity constant of potassium salt is larger than that of sodium salt.

3. The reaction velocity of potassium monochloracetate with potassium hydroxide is retarded by the presence of another salt (i.e. KNO_3).

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