A Study of the Kinetics of the Reaction between Hydrogen Peroxide and the Sodium Salt of *p*-Toluenesulfonchloramide (Chloramine T)

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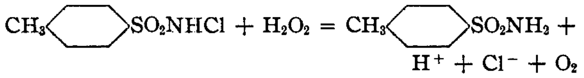
Introduction.—In the potentiometric titration of hydrogen peroxide using chloramine T the authors found that a measurable time elapsed before the stoichiometric end-point was reached. This suggested the idea that it might be worth while to study the rate of this reaction.

Reagents and Procedure.—The hydrogen peroxide was of reagent grade and contained 3.6% H_2O_2 (by weight). The chloramine T conformed to the requirements of the U. S. P. and was standardized before use by means of potassium iodide and thiosulfate.[4]

In the experimental runs various ratios of standard hydrogen peroxide and chloramine T were taken and diluted to a total volume of 100 cc. the temperature being constant at 25 ± 0.01°. The mixture contained 3 cc. of 5.298 *M* hydrochloric acid in each run, this amount of acid being below that necessary to cause precipitation of the chloramine T as the dichloride which is sparingly soluble. The reaction was considered to begin on the addition of the acid, a fact already confirmed by previous experiment. Ten-cc. samples were removed from time to time and added to known amounts of 0.01 *N* permanganate acidified with sulfuric acid to stop the reaction. The precise end-point was determined by adding the permanganate dropwise. The experimental results for a series of runs are shown in Table I.

Theory and Calculations.—From the equation of the over-all reaction



it would seem that a bimolecular process takes place. The experimental results show that this is not so. Furthermore, the reaction is so rapid at the beginning that concordant results are extremely difficult to obtain. To determine the rate of the reaction the method of logistic function was used.[5] The differential equation of the logistic function used by Reed and Berkson is of the type

$$dy/dt = k(M - y)(N - y)$$

TABLE I

t, min.	Normality H_2O_2	*y*
Run 15. $a = 0.01064$ molal H_2O_2.		$b = 0.00625$ molal ClT
35	0.01228	0.00450
60	.01150	.00489
90	.01110	.00509
117	.01060	.00534
150	.01028	.00550
178	.01017	.00555
216	.01009	.00559
240	.01002	.00563
262	.00997	.00565
Mean value of $k = 1.60 \times 10^{-2}$		
Run 17. $a = 0.00735$ molal H_2O_2.		$b = 0.00625$ molal ClT
25	0.00705	0.00382
59	.00609	.00430
99	.00512	.00479
126	.00455	.00507
153	.00425	.00522
182	.00400	.00537
Mean value of $k = 1.75 \times 10^{-2}$		
Run 19. $a = 0.0059$ molal H_2O_2.		$b = 0.00750$ molal ClT
29	0.00460	0.00360
53	.00375	.00402
83	.00324	.00428
109	.00274	.00453
141	.00231	.00474
167	.00212	.00484
Mean value of $k = 1.48 \times 10^{-2}$.		$N = 0.00665$
Run 23. $a = 0.00490$ molal H_2O_2.		$b = 0.00625$ molal ClT
29	0.00357	0.00311
59	.00270	.00355
101	.00179	.00401
127	.00144	.00418
155	.00131	.00425
184	.00114	.00435
Mean value of $k = 1.72 \times 10^{-2}$.		$N = 0.00569$
Run 24. $a = 0.00590$ molal H_2O_2.		$b = 0.005$ molal ClT
24	0.00512	0.00334
55	.00459	.00361
85	.00424	.00378
111	.00390	.00395
143	.00362	.00409
170	.00340	.00420
Mean value of $k = 1.64 \times 10^{-2}$.		$N = 0.00460$

It was discovered in the determination of the reaction rate that when the concentration of chloramine T was held constant, the hydrogen peroxide being varied, the reaction was approximately bimolecular. Therefore in the above differential equation $M = a =$ initial concentra-

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[4] Kolthoff and Furman, "Potentiometric Titrations," John Wiley & Sons, New York, N. Y., p. 317.

[5] Reed and Berkson, *J. Phys. Chem.*, **33**, 760 (1929).

tion of hydrogen peroxide. It was found that no value of N could satisfy the equation. A modified function was adopted such that

$$\ln \frac{(N-y)^N}{(a-y)^a} + \ln C = (a-N)kt \qquad (1)$$

The differential equation of the function is seen to be

$$\frac{dy}{dt} = \frac{k(a-y)(N-y)}{y}$$

where a is initial $[H_2O_2]$ as before, and y = the concentration of NH_2T (*i. e.*, *p*-toluenesulfonamide) at any time t, also equal to the amount of hydrogen peroxide or ClT (*i. e.*, chloramine T) decomposed at time t. The evaluation of N is as follows. In equation (1) let

$$Y = \ln \frac{(N-y)^N}{(a-y)^a} = N \ln (N-y) - a \ln (a-y)$$

then if Y is plotted against t for various assumed values of N, the one value of N which satisfies the equation will give a straight line as shown in Fig. 1. The slope of the line × 2.303 divided by $(a-N)$ gives the value of k, the velocity constant.

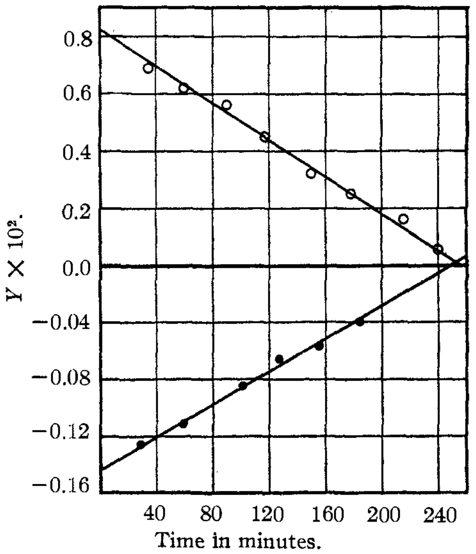
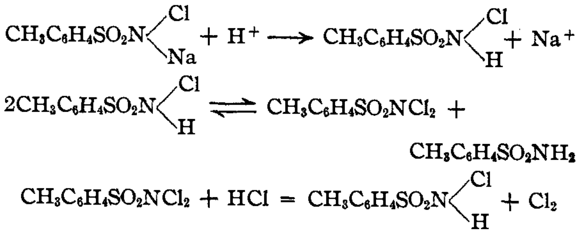


Fig. 1.

The Physical Meaning of N.—It has already been shown that N is independent of a and therefore N must be a function of b, where b is initial concentration of chloramine T. The values of b used and the corresponding values of N as determined are

b = ClT m./l.	N (detd.)
6.25×10^{-3}	5.69×10^{-3}
5.0×10^{-3}	4.6×10^{-3}
7.5×10^{-3}	6.65×10^{-3}

It is seen that N, the concentration of the substance participating in the reaction, is always less than the concentration of the chloramine T. This suggests that there are some opposing simultaneous reactions taking place. According to the work of Chattaway,[6] Orton and Jones,[7] and others, the sodium salt of chloramine T when placed in acid solution containing hydrochloric acid undergoes a series of reactions



$$CH_3C_6H_4SO_2N{<}^{Cl}_{Na} + H^+ \longrightarrow CH_3C_6H_4SO_2N{<}^{Cl}_{H} + Na^+$$

$$2CH_3C_6H_4SO_2N{<}^{Cl}_{H} \rightleftharpoons CH_3C_6H_4SO_2NCl_2 + CH_3C_6H_4SO_2NH_2$$

$$CH_3C_6H_4SO_2NCl_2 + HCl = CH_3C_6H_4SO_2N{<}^{Cl}_{H} + Cl_2$$

From which it is seen that the addition of hydrogen peroxide to the above-mentioned hydrochloric

$$Cl_2 + H_2O = H^+ + Cl^- + HOCl$$

$$HOCl + H_2O_2 \longrightarrow H_2O + HCl + O_2\uparrow$$

acid solution causes reaction in the usual way. It is apparent from our data as well as the reactions given above that not all of the chloramine T enters the reaction at the concentration of hydrochloric acid used. It becomes necessary therefore to designate the chloramine T entering the reaction as "active," its concentration at any time being $(N-y)$, where N is the total active concentration of chloramine T at the beginning of the reaction. N is a function of b and the functional relationship is expressed by $K = N^2/(b-N)$, where K is a mathematical constant. For the three values of N already quoted K is found to be 5.77×10^{-2}, 5.30×10^{-2}, 5.21×10^{-2} and $K_{(\text{mean})} = 5.43 \times 10^{-2}$.

The differential equation expressing the rate of decomposition of hydrogen peroxide in the presence of chloramine T may therefore be represented by the relation

$$-\frac{d[H_2O_2]}{dt} = k\,\frac{[H_2O_2][ClT]_{\text{act.}}}{[NH_2T]}$$

Summary

1. A differential equation expressing the overall rate of reaction between chloramine T and hydrogen peroxide at constant $[H^+]$ and $[Cl^-]$ has been developed.

2. A mathematical constant expressing the active chloramine T concentration in solutions of varying concentration at fixed $[H^+]$ and $[Cl^-]$ has been calculated.

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[6] Chattaway, *J. Chem. Soc.*, **87**, 128 (1905).

[7] Orton and Jones, *ibid.*, **95**, 1456 (1909).