portion of the system has hysteresis which is so slow that a spurious balance is obtained. In the study of paramagnetic systems at low temperatures the onset of coöperative phenomena, such as ferromagnetism, should be rather gradual. For this reason, it seems unlikely that such severe hysteresis as that mentioned above could develop without observable effects due to its initial stages.

Summary

A fluxmeter for measuring the reversible adiabatic magnetic susceptibility in the presence of large fields has been devised and tested.

Equations relating the observed magnetic induction to the susceptibility of the sample have been given.

Cadmium–zinc solder has been suggested for use in magnetic apparatus at the temperature of liquid helium where the superconductive properties of ordinary solder are objectionable if sensitive measurements are desired.

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[CONTRIBUTION FROM THE DEPARTMENT OF SANITARY ENGINEERING, GRADUATE SCHOOL OF ENGINEERING, HARVARD UNIVERSITY]

Kinetic Studies on the Chloramines. I. The Rates of Formation of Monochloramine, N-Chlormethylamine and N-Chlordimethylamine[1]

BY IRA WEIL AND J. CARRELL MORRIS

In aqueous solution, chlorine or hypochlorites react readily with ammonia or ammonium ions to give a series of products—monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3).[2] Presumably these products are formed successively so that the reactions that occur may be represented stoichiometrically by the equations

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \quad (1)$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O \quad (2)$$

$$HOCl + NHCl_2 \longrightarrow NCl_3 + H_2O \quad (3)$$

These reactions are of great practical importance in the disinfection of water supplies with chlorine or hypochlorites and in addition, as will be shown, are of considerable interest from the viewpoint of theoretical solution kinetics. Hence, a detailed study of their rates has been undertaken.

The present paper deals principally with the first of these reactions—the rate of formation of monochloramine. The rates of similar reactions of aqueous chlorine with methylamine and dimethylamine or their salts have also been studied to aid in the interpretation of the results obtained with ammonia.

The interaction of aqueous chlorine and ammonia or amines is so rapid that the rate is measurable by ordinary techniques only at very low concentrations of the order of $10^{-5}M$. At such dilutions, provided large concentrations of H^+ or Cl^- are not present, the hydrolysis of chlorine to hypochlorous acid is virtually complete (better than 99.99% in all the experiments). Hence, it is presumably HOCl or OCl^- which takes part in the reactions—as shown by the equations. This conclusion is substantiated by the data presented later.

The progress of the reactions was generally followed by measuring colorimetrically the decrease in the concentration of unreacted $HOCl + OCl^-$ with time. This gives the rate of formation of monochloramine if reactions (2) and (3) do not occur simultaneously. In order to minimize the interference by these succeeding reactions, all of the experiments were carried out in the presence of a considerable excess of ammonia or ammonium ions, and determinations of the rate were based primarily on results for the initial period of the reaction.

As a check on the sufficiency of these precautions some experiments were conducted by a different technique. It was possible, under certain conditions, to follow the reaction spectrophotometrically, using the increasing intensity of the NH_2Cl band at 245 mμ[3,4] as a direct measure of its rate of formation. The two methods gave results in good agreement.

The rate of reaction of aqueous chlorine with dimethylamine provided another check that the measured rates of disappearance of hypochlorite were equal to the rates of formation of monochloramine. With dimethylamine only a monochloro derivative results, its formation corresponding to the reaction

$$(CH_3)_2NH + HOCl \longrightarrow (CH_3)_2NCl + H_2O \quad (4)$$

Parallel results were obtained for the reactions of aqueous chlorine with ammonia and with dimethylamine, a fact which gives added assurance that the observed rates for the ammonia reaction are to be attributed to reaction (1).

Experimental

Reagents.—For experiments with very low concentrations of chlorine it is essential that the reaction medium (distilled water or salt solution) be free of all traces of

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[1] This paper is based on work performed under Contract No. W-44-009 eng-463 for the Engineer Research and Development Laboratories, U. S. Army.

[2] See Berliner, *J. Am. Water Works Assoc.*, **23**, 1320 (1931), for a review of the chemistry of these compounds.

[3] Metcalf, *J. Chem. Soc.*, 148 (1942).

[4] Burden, Doctoral Thesis, 1948, Graduate School of Engineering, Harvard University.

materials capable of reducing chlorine or hypochlorite. Hence, the water or solutions used for the experiments were subjected to a preliminary treatment to produce so-called "chlorine-demand-free" water.[5] Sufficient chlorine was added to carboys of distilled water and to the stock solutions of salts to give residual concentrations of $5 \times 10^{-5}M$, and the chlorinated solutions were stored in the dark for two days or more. Sufficient sodium sulfite was then added to reduce the chlorine concentration to about $10^{-6}M$. The last traces of chlorine were removed by boiling the water or salt solution for fifteen minutes immediately before use.

Strong chlorine solutions were prepared by bubbling tank chlorine gas through distilled water until the concentration was approximately 0.01 M. Working stock solutions were prepared from these by dilution to 5×10^{-4} M. The dilute stock solutions were standardized before each use by titrating suitable portions with 0.01 M sodium thiosulfate after addition of sodium iodide and starch solution.

Stock solutions of C. P. ammonium chloride and amine hydrochlorides (Eastman Kodak Company) were prepared by dissolving in chlorine-demand-free water appropriate weighed quantities of the salts to give 5×10^{-3} M solutions. The concentrations of the solutions were checked by Kjeldahl distillation and titration.

The *o*-tolidine reagent was prepared by dissolving 1.35 g. of *o*-tolidine dihydrochloride (Eastman Kodak Company) in 500 ml. of distilled water and mixing with 500 ml. of 3.6 M HCl.[6] Sodium arsenite solution was prepared by dissolving 5 g. of reagent grade sodium arsenite in a liter of distilled water.

Determination of Total Active Chlorine.—For the determination of "total active chlorine" (hypochlorites + chloramines) in the test solutions, a form of the standard *o*-tolidine test was employed.[6] To 3 ml. of the *o*-tolidine test solution in a 125-ml. erlenmeyer flask, 50 ml. of the test solution was added. After four minutes, the intensity of the yellow color was measured at 435 mμ with a Coleman Universal Spectrophotometer which had previously been calibrated with chlorine solutions of known concentration. The test is sufficiently sensitive so that, with the standard 13 mm. cells of the Coleman instrument, the transmittancy at 435 mμ is reduced to 90% for 10^{-6} M chlorine concentration.

Determinations of this type were made on the chlorine test solutions before mixing with the ammonia or amine solutions and, in the case of the ammonia studies, were also carried out at the conclusion of the tests to measure any losses of active chlorine through volatilization or reduction. The observed loss was never greater than 2% of the initial concentration. Corrections for this loss were applied. In the experiments with methyl and dimethylamines, the final test could not be applied because the oxidation of *o*-tolidine by methylchloramine and dimethylchloramine is not complete before fading of the color becomes significant.

Determination of Unreacted HOCl + OCl⁻.—The *o*-tolidine-arsenite procedure[6,7] was used for the evaluation of unreacted hypochlorite during the course of the runs. This test is based upon the observations that hypochlorite reacts much more rapidly with *o*-tolidine than do the chloramines, and that the addition of sodium arsenite arrests further oxidation of the *o*-tolidine by hypochlorite or chloramines.

In a series of blank tests it was established that the reaction between hypochlorites and *o*-tolidine is complete under the test conditions within three seconds at temperatures from 5 to 40°. Hence, the following procedure was adopted. Three ml. of the *o*-tolidine test solution was placed in a 125-ml. erlenmeyer flask, and at the desired time a 50-ml. sample was poured very rapidly into the flask and swirled vigorously. After three seconds, 3 ml. of sodium arsenite reagent was added quickly with shaking and the transmittancy of the sample was determined.

Although the reaction of *o*-tolidine with chloramines is slower than with hypochlorite, measurable amounts do react during the three-second interval. Therefore, a comprehensive study of the rate of reaction between *o*-tolidine and the ammonia-chloramines was necessary so that appropriate correction factors might be applied to the observed unreacted chlorine concentrations.[8] It was found that 9% of the ammonia-chloramines present reacted with *o*-tolidine within three seconds at 25°, when the standard test procedure was followed. This correction was applied to the observed data at that temperature. Similar factors for other temperatures were also determined and employed.

Similar tests with methylchloramine and dimethylchloramine showed that much less than 1% of the chloramines present reacted during the three-second interval, so that corrections were not required for studies with these chloramines.

Colorimetric Rate Measurements.—An appropriate volume of chlorine-demand-free solvent (generally about 500 ml.) at the required temperature was adjusted to the desired *p*H by the addition of hydrogen chloride or sodium hydroxide, and was then divided into two portions. To one was added a sufficient quantity of ammonia or amine solution to give twice the concentration desired in the reaction vessel. To the other was added a similar quantity of stock chlorine solution, the concentration of this solution then being checked by the *o*-tolidine test.

Equal volumes of the two solutions were then poured rapidly and simultaneously into a large Pyrex beaker, thus insuring almost instantaneous mixing. Periodically, 50-ml. samples were withdrawn and tested for unreacted hypochlorite by the *o*-tolidine-arsenite procedure.

The *p*H of the reacting solution was determined with a Beckman (Model G) *p*H meter at the beginning and end of each test run by means of a glass electrode which was calibrated against Bureau of Standards buffers. In every case the *p*H was constant within the limit of error of the measurement, 0.02 *p*H unit.

Spectrophotometric Rate Measurements.—A Beckman ultraviolet spectrophotometer (Model DU) was employed for the direct determination of the rate of formation of monochloramine. Samples of reaction mixtures, prepared as in the preceding section, were placed in a 10-cm. quartz absorption cell and transmittancies were measured periodically at 295 and 245 mμ, wave lengths of maximum absorbancy for OCl^- and NH_2Cl, respectively. Previous spectral studies on these compounds[3,4] had established their absorption coefficients.

Results

Reaction of Ammonia and Hypochlorous Acid.

—The formation of monochloramine appears to be a bimolecular reaction in accordance with equation (1). Data for a *p*H of 12.05, at which the order was most easily determined, are shown in Table I. Second-order behavior within the estimated precision of the measurements (±10% in the rate constants) is shown for the course of each run as well as for different runs with varying initial concentrations.

The results of a similar experiment at *p*H 12.30 are shown in Table II. In this experiment the rate of reaction was determined by measuring the change in intensity of the ultraviolet absorption bands for OCl^- and NH_2Cl. The difference between the average values of the rate constant for this experiment and for those shown in Table I is to be attributed to the difference in *p*H.

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[5] Butterfield, Wattie, Megregian and Chambers, *Public Health Reports*, **58**, 1837 (1943).

[6] "Standard Methods for the Examination of Water and Sewage," Am. Public Health Assoc., 9th edition, 1946, pp. 92-102.

[7] Hallinan, *J. Am. Water Works Assoc.*, **36**, 296 (1944).

[8] It is planned to publish detailed results of this study at a later date.

TABLE I

RATE OF FORMATION OF MONOCHLORAMINE AT pH 12.05

Temperature 25 ± 0.5°; colorimetric determination.

Time, min.	Unreacted hypochlorite, C, mole/l. × 10^5	$\ln \frac{C_0N}{N_0C}$	$k_{obs} \times 10^{-3}$ [a] (l./mole-min.)
1. Initial hypochlorite, $C_0 = 0.72 \times 10^{-5}$ mole/l. Initial ammonia, $N_0 = 1.44 \times 10^{-5}$ mole/l.			
1.00	0.646	0.055	7.6
2.00	.587	.105	7.3
3.00	.542	.153	7.1
4.00	.491	.210	7.3
5.00	.447	.267	7.4
2. $C_0 = 1.44 \times 10^{-5}$ mole/l.; $N_0 = 4.32 \times 10^{-5}$ mole/l.			
1.00	1.048	0.223	7.7
2.00	0.802	.425	7.4
3.00	.617	.637	7.4
4.00	.482	.842	7.3
5.00	.382	1.044	7.3
3. $C_0 = 1.44 \times 10^{-5}$ mole/l.; $N_0 = 7.20 \times 10^{-5}$ mole/l.			
1.00	0.850	0.445	7.7
2.00	.532	0.863	7.5
3.00	.352	1.247	7.2
4.00	.231	1.645	7.1
5.00	.145	2.099	7.3
4. $C_0 = 2.88 \times 10^{-5}$ mole/l.; $N_0 = 7.20 \times 10^{-5}$ mole/l.			
1.00	1.785	0.315	7.3
2.00	1.130	.656	7.6
3.00	0.806	.933	7.2
4.00	0.573	1.228	7.1
			Ave. 7.4 ± 0.2

[a] Values of k_{obs} in this and the other tables were calculated from the integral form of the general second-order equation, *i. e.*

$$k_{obs} = \frac{1}{t(N_0 - Co)} \ln \frac{C_0N}{N_0C}$$

TABLE II

SPECTROPHOTOMETRIC DETERMINATION OF RATE OF FORMATION OF MONOCHLORAMINE AT pH 12.30

Temperature 25.0 ± 0.5°; $C_0 = 3.00 \times 10^{-5}$ mole/l.; $N_0 = 6.00 \times 10^{-5}$ mole/l.

Time, min.	Transmittancy		Unreacted hypochlorite mole/l. × 10^5		$k_{obs} \times 10^{-3}$ 1/mole min.	
	245 mμ	295 mμ	245 mμ	295 mμ	245 mμ	295 mμ
2.00	...	0.849	..	2.05	...	3.5
2.50	0.873	.856	1.87	1.94	3.6	3.3
3.00	.856	...	1.67	..	3.8	...
3.25	...	.873	..	1.68	...	3.5
3.50	.842	.879	1.51	1.59	3.9	3.5
4.00	.832	.891	1.39	1.40	3.8	3.8
5.00	.810	...	1.12	..	4.0	...
					Av. 3.7 ± 0.2	

Although the rate of formation of monochloramine is second-order at any fixed pH value, it is markedly dependent on the hydrogen-ion concentration. This is shown in Table III, which lists in the second column values of the second-order rate constant obtained at various pH values. In Fig. 1, these values have been plotted against the pH. It was impossible to determine rates between pH 6.5 and 10 because of the rapidity of the reaction in this range.

TABLE III

VARIATION OF RATE OF FORMATION OF NH_2Cl WITH pH

Temperature 25.0 ± 0.5°; $C_0 = 1.13 \times 10^{-5}$ mole/l.; $N_0 = 2.26 \times 10^{-5}$ mole/l.

pH	$k_{obs} \times 10^{-3}$ 1/mole min.	Ionic strength	$k_1 \times 10^{-8}$ 1/mole min.
4.60	8.9	0.0001	3.7
4.71	13.0	.0001	4.1
6.11	220.0	.0001	3.5
6.49	580.0	.0001	3.4
10.95	92.0	.0011	3.4
12.05[a]	7.4	.012	3.9
12.23	5.8	.015	4.0
12.30[b]	3.7	.021	3.8

[a] Average of runs in Table I. [b] Determined by spectrophotometric method, see Table II.

The temperature dependence of the reaction rate was determined at two pH values—one in the low pH range at pH 4.58 and one in the high pH range at pH 11.70. Bimolecular rate constants calculated from the data are shown in the second column of Table IV. Despite the rapidity of the reaction, the observed temperature dependence is quite great. Apparent activation energies are 16.5 kcal. at pH 4.58 and 11.0 kcal. at pH 11.70.

TABLE IV

TEMPERATURE DEPENDENCE OF RATE OF FORMATION OF NH_2Cl

$C_0 = 1.13 \times 10^{-5}$ mole/l.; $N_0 = 2.26 \times 10^{-5}$ mole/l.

Temp., °C.	$k_{obs} \times 10^{-3}$ l./mole min.	$k_1 \times 10^{-8}$ l./mole min.
	A. pH 4.58	
5.9	1.23	2.5
14.8	2.9	3.0
25.3	7.6	3.5
37.3	21.2	4.3
	B. $[OH^-] = 5.3 \times 10^{-3}$	
5.8	5.1	2.8
16.7	9.6	3.2
31.0	18.4	3.6
35.0	28.2	3.9

Reactions with Methylamine and Dimethylamine.—The reactions between aqueous chlorine and solutions of methylamine or dimethylamine were also found to be second order by experiments similar to those on the formation of NH_2Cl. The reaction with dimethylamine is represented by equation (4) and that with methylamine by the equation

$$CH_3NH_2 + HOCl \longrightarrow CH_3NHCl + H_2O \quad (5)$$

The rates of formation of CH_3NHCl and $(CH_3)_2NCl$ vary with pH in the same manner as the formation of NH_2Cl. This is shown in Table V for CH_3NHCl and in Table VI for $(CH_3)_2NCl$, the values in the second column being the observed second-order rate constants.

TABLE V

THE RATE OF FORMATION OF CH_3NHCl AT VARIOUS *p*H VALUES

Temperature 25.0 ± 0.5°; hypochlorite, $C_0 = 1.13 \times 10^{-5}$ mole/l.; methylamine, $N_0 = 2.26 \times 10^{-5}$ mole/l.

*p*H	$k_{obs} \times 10^{-3}$ l./mole min.	Ionic strength	$k_2 \times 10^{-10}$ l./mole min.
4.33	15.1	0.0001	3.0
4.87	53.0	.0001	3.1
5.81	442.0	.0001	3.0
12.42	186.0	.026	2.6
12.67	114.0	.046	3.2
12.88	64.0	.081	3.4

TABLE VI

THE RATE OF FORMATION OF $(CH_3)_2NCl$ AT VARIOUS *p*H VALUES

Temperature 25.0 ± 0.5°; hypochlorite, $C_0 = 1.13 \times 10^{-5}$ mole/l.; dimethylamine, $N_0 = 2.26 \times 10^{-5}$ mole/l.

*p*H	$k_{obs} \times 10^{-3}$ l./mole min.	Ionic strength	$k_3 \times 10^{-10}$ l./mole min.
4.09	5.2	0.0001	2.6
4.97	50.0	.0001	3.2
5.60	210.0	.0001	3.2
12.45	152.0	.030	2.5
12.74	82.0	.056	2.9
12.87	65.0	.076	3.3

In Table VII the temperature dependence of the rates of formation of CH_3NHCl and $(CH_3)_2NCl$ in the high *p*H range is shown. The observed rate constants in the second column give an apparent activation energy of 13.8 kcal. for CH_3NHCl formation and of 10.0 kcal. for $(CH_3)_2NCl$ formation.

TABLE VII

TEMPERATURE DEPENDENCE OF RATES OF FORMATION OF CH_3NHCl AND $(CH_3)_2NCl$

Initial concentrations; hypochlorite, $C_0 = 1.13 \times 10^{-5}$ mole/l.; amine, $N_0 = 2.26 \times 10^{-5}$ mole/l.

Temp., °C.	$k_{obs} \times 10^{-3}$ l./mole min.	(k_2 or k_3) $\times 10^{-10}$ l./mole min.
A.	CH_3NHCl, $[OH^-] = 0.12$	
6.5	15.3	1.8
11.8	22.4	2.1
15.6	29.4	2.3
21.2	48.0	2.6
24.8	66.5	3.0
B.	$(CH_3)_2NCl$, $[OH^-] = 0.12$	
6.3	21.3	2.6
11.2	27.8	2.7
14.2	32.5	2.8
21.0	51.8	2.9
24.6	62.7	3.0

Discussion

Variation of Rate with *p*H.—The characteristic changes in the rates of formation of NH_2Cl, CH_3NHCl and $(CH_3)_2NCl$ with the hydrogen-ion concentration of the solution can be accounted for in two ways on the reasonable assumption that the changes correspond to alterations in the concentrations of the species participating in the reaction.

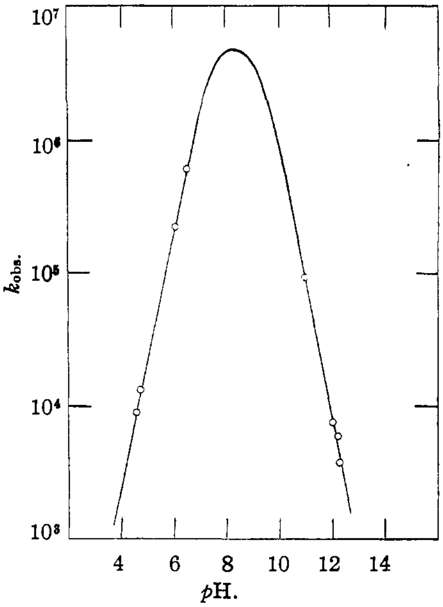

Fig. 1.—The *p*H dependence of the observed rate for the NH_3–$HOCl$ reaction. The theoretical dependence is shown by the solid line.

On the one hand, it may be assumed that the reaction is between non-ionized HOCl molecules and non-ionized NH_3, CH_3NH_2 or $(CH_3)_2NH$ as shown in equations (1), (4) and (5). The increase in rate from *p*H 4 to 6 can be considered to result from the greater fraction of the analytical ammonia or amine concentration present as the free base at *p*H 6. Similarly, the decrease in rate from *p*H 10 to 12 can be attributed to the ionization of the HOCl. This approach predicts a tenfold increase in rate per *p*H unit in the *p*H range below 6, and a tenfold decrease per *p*H unit above *p*H 10. Figure 1 shows that these predictions are in accord with the observed slopes.

However, if one assumes that the reactions are completely ionic according to the equations

$$NH_4^+ + OCl^- \longrightarrow NH_2Cl + H_2O \quad (6)$$

$$CH_3NH_3^+ + OCl^- \longrightarrow CH_3NHCl + H_2O \quad (7)$$

$$(CH_3)_2NH_2^+ + OCl^- \longrightarrow (CH_3)_2NCl + H_2O \quad (8)$$

then the variation in rate with *p*H can also be accounted for. On this basis, the increase in rate from *p*H 4 to 6 corresponds to the increasing fraction of the analytical chlorine present as OCl^- and the decreasing rate from *p*H 10 to 12 to the decreasing fraction of the analytical ammonia or amine which is present as NH_4^+, $CH_3NH_3^+$ or $(CH_3)_2NH_2^+$.

Other possible mechanisms, such as those involving $NH_3 + OCl^-$, $NH_4^+ + HOCl$, $Cl_2 + NH_3$, etc., are incompatible with the change in rate with *p*H.

A priori, it would seem possible to differentiate between the alternative mechanisms by means of a primary salt effect. However, closer examination leads to the conclusion that the mechanisms are kinetically indistinguishable. The rate of the ammonia reaction can be written as

$$v = k_1[\mathrm{NH_3}][\mathrm{HOCl}]f_{\mathrm{NH_3}}f_{\mathrm{HOCl}}/f_{\mathrm{x}} \qquad (9)$$

or

$$v = k_1'[\mathrm{NH_4^+}][\mathrm{OCl^-}]f_{\mathrm{NH_4^+}}f_{\mathrm{OCl^-}}/f_{\mathrm{x}} \qquad (10)$$

for the non-ionic and ionic mechanisms, respectively. The terms $f_{\mathrm{NH_3}}$, f_{HOCl}, $f_{\mathrm{NH_4^+}}$ and $f_{\mathrm{OCl^-}}$ represent the activity coefficients of the various reacting substances and f_{x} is that of the activated complex. If the expressions for the dissociation constants of HOCl and $\mathrm{NH_3}$

$$K_{\mathrm{a}} = ([\mathrm{H^+}][\mathrm{OCl^-}]/[\mathrm{HOCl}])f_{\mathrm{H^+}}f_{\mathrm{OCl^-}}/f_{\mathrm{HOCl}} \qquad (11)$$

$$K_{\mathrm{b}} = ([\mathrm{NH_4^+}][\mathrm{OH^-}]/[\mathrm{NH_3}])f_{\mathrm{OH^-}}f_{\mathrm{NH_4^+}}/f_{\mathrm{NH_3}} \qquad (12)$$

are substituted in equation (9), the equation

$$v = (k_1K_{\mathrm{w}}/K_{\mathrm{a}}K_{\mathrm{b}})[\mathrm{NH_4^+}][\mathrm{OCl^-}]f_{\mathrm{NH_4^+}}f_{\mathrm{OCl^-}}/f_{\mathrm{x}} \qquad (13)$$

results, where K_{w} is the activity product of water. Equation (13) reduces to equation (10) for

$$k_1' = k_1K_{\mathrm{w}}/K_{\mathrm{a}}K_{\mathrm{b}} \qquad (14)$$

Hence, changes in ionic strength will have the same influence whichever mechanism is operative.

Specific Rate Constant.—Expressions can be derived to calculate the specific rate constant for the formation of monochloramine for either the ionic or non-ionic mechanism. Since the relationship between the two constants is given in equation (14), it is sufficient to derive the expression for only one of the mechanisms.

Let C be the analytical chlorine concentration and N be the analytical ammonia concentration. Then

$$C = [\mathrm{HOCl}] + [\mathrm{OCl^-}] \qquad (15)$$

and

$$N = [\mathrm{NH_3}] + [\mathrm{NH_4^+}] \qquad (16)$$

To obtain the non-ionic rate constant, these equations are combined with equations (11) and (12) to give

$$C = [\mathrm{HOCl}][1 + (K_{\mathrm{a}}/[\mathrm{H^+}])(f_{\mathrm{HOCl}}/f_{\mathrm{OCl^-}}f_{\mathrm{H^+}})] \qquad (17)$$

$$N = [\mathrm{NH_3}][1 + (K_{\mathrm{b}}/[\mathrm{OH^-}])(f_{\mathrm{NH_3}}/f_{\mathrm{NH^+_4}}f_{\mathrm{OH^-}})] \qquad (18)$$

The observed rate of the reaction can be written as

$$-\mathrm{d}C/\mathrm{d}t = k_1[\mathrm{NH_3}][\mathrm{HOCl}]f_{\mathrm{NH_3}}f_{\mathrm{HOCl}}/f_{\mathrm{x}} \qquad (19)$$

Substitution of the values for $[\mathrm{NH_3}]$ and [HOCl] yields

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_1CN\,f_{\mathrm{NH_3}}f_{\mathrm{HOCl}}/f_{\mathrm{x}}}{\left(1 + \frac{K_{\mathrm{a}}}{[\mathrm{H^+}]}\,\frac{f_{\mathrm{HOCl}}}{f_{\mathrm{OCl^-}}f_{\mathrm{H^+}}}\right)\left(1 + \frac{K_{\mathrm{b}}}{[\mathrm{OH^-}]}\,\frac{f_{\mathrm{NH_3}}}{f_{\mathrm{NH_4^+}}f_{\mathrm{OH^-}}}\right)} \qquad (20)$$

The activity coefficient terms for the neutral molecules are important only for the study of the reaction in different media. In dilute water solution they may be taken as unity. In addition the activity coefficients of all the monovalent ions may be considered equal. Hence

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{k_1CN}{(1 + K_{\mathrm{a}}/[\mathrm{H^+}]f^2)(1 + K_{\mathrm{b}}/[\mathrm{OH^-}]f^2)f_{\mathrm{x}}} \qquad (21)$$

The observed rate constants were obtained from the equation

$$-\mathrm{d}C/\mathrm{d}t = k_{\mathrm{obs}}CN \qquad (22)$$

This gives

$$k_1/f_{\mathrm{x}} = k_{\mathrm{obs}}(1 + K_{\mathrm{a}}/[\mathrm{H^+}]f^2)(1 + K_{\mathrm{b}}/[\mathrm{OH^-}]f^2) \qquad (23)$$

or

$$k_1/f_{\mathrm{x}} = (k_{\mathrm{obs}}/f^2)(f^2 + K_{\mathrm{a}}K_{\mathrm{b}}/K_{\mathrm{w}} + K_{\mathrm{a}}/[\mathrm{H^+}] + K_{\mathrm{b}}[\mathrm{H^+}]f^2/K_{\mathrm{w}}) \qquad (24)$$

At 25°, the values for the dissociation constants are: K_{a}, 3.7×10^{-8}(9); K_{b}, 1.65×10^{-5}(10); K_{w}, 1.01×10^{-14}.(11) Substitution of these values in equation (24) gives

$$k_1/f_{\mathrm{x}} = (k_{\mathrm{obs}}/f^2)(f^2 + 60.4 + 3.7 \times 10^{-8}/[\mathrm{H^+}] + 1.63 \times 10^{9}[\mathrm{H^+}]f^2) \qquad (25)$$

According to the mechanisms discussed, the activated complex is uncharged. This will also be shown to be true on the basis of ionic strength data. Therefore, f_{x} may be assumed equal to 1 in dilute solutions. Values of k_1, calculated from equation (25) are shown in the last column of Table III. The values of the activity coefficient have been computed from the Debye–Hückel limiting law, $-\log f = 0.5\sqrt{\mu}$. An average result of $(3.7 \pm 0.2) \times 10^{8}$ at 25° with units in moles per liter and minutes is obtained for k_1. The theoretical variation of k_{obs} with *p*H, shown by the curve in Fig. 1, has been obtained by substituting this value into equation (25).

Similar equations are obtained for the methylamine and dimethylamine reactions. At 25°, the ionization constants being 4.25×10^{-4} and 6.0×10^{-4}, respectively,[12] the equations become

$$k_2/f_{\mathrm{x}} = (k_{\mathrm{obs}}/f^2)(f^2 + 769 + 3.7 \times 10^{-8}/[\mathrm{H^+}] + 4.21 \times 10^{10}[\mathrm{H^+}]f^2) \qquad (26)$$

and

$$k_3/f_{\mathrm{x}} = (k_{\mathrm{obs}}/f^2)(f^2 + 1090 + 3.7 \times 10^{-8}/[\mathrm{H^+}] + 5.94 \times 10^{10}[\mathrm{H^+}]f^2) \qquad (27)$$

Values of k_2 and k_3, evaluated by means of these equations, are shown in the last columns of Tables V and VI. Good constancy over the whole *p*H range is again observed and substantiates the proposed interpretation.

Effect of Ionic Strength.—The proposed reaction mechanisms can be further tested by observing the effect of changes in ionic strength on the rate. At high *p*H values, equation (23) reduces with high precision to

$$k_1/f_{\mathrm{x}} = k_{\mathrm{obs}}K_{\mathrm{a}}/[\mathrm{H^+}]f^2 = k_{\mathrm{obs}}K_{\mathrm{a}}[\mathrm{OH^-}]/K_{\mathrm{w}} \qquad (28)$$

or

$$k_{\mathrm{obs}} = k_1K_{\mathrm{w}}/K_{\mathrm{a}}[\mathrm{OH^-}]f_{\mathrm{x}} \qquad (29)$$

Therefore, if the hydroxyl ion *concentration* is kept constant, there should be no variation in the rate

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(9) Final Report, Contract OEM-cmr 251, National Research Council December 31, 1945.

(10) Everett and Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A169**, 190 (1938).

(11) Harned and Geary, THIS JOURNAL, **59**, 2032 (1937).

(12) Everett and Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941).

with ionic strength provided f_x is uncharged as predicted. Results of experiments to test this hypothesis are shown in Table VIII.

TABLE VIII

VARIATION OF RATE OF FORMATION OF NH_2Cl WITH IONIC STRENGTH

Temperature 25.0 ± 0.5°; $[OH^-] = 7.5 \times 10^{-3}$ for all tests; KNO_3 added as neutral salt. Initial concentrations hypochlorite, $C_0 = 1.13 \times 10^{-5}\ M$; ammonia, $N_0 = 2.26 \times 10^{-5}\ M$

Ionic strength, μ	0.01	0.03	0.05	0.11	0.21
$k_{obs} \times 10^{-8}$	14.0	13.6	13.3	13.1	13.6

No change in rate greater than experimental error was found, in agreement with equation (29).

Temperature Effects.—The observed temperature dependence of the reaction rates is a composite of many factors, as shown by equation (24). In order to determine the true Arrhenius activation energy for the reactions, it is necessary to take account of the variations of K_a, K_b and K_w with temperature.

At *p*H 4.6, equation (24) approximates quite closely to

$$k_1 = k_{obs}K_b[H^+]/K_w \qquad (30)$$

At *p*H values above 11, equation (29) is applicable. Similar equations hold for k_2 and k_3. These equations have been used for the evaluation of k_1, k_2 and k_3 at the various temperatures, by substituting the appropriate interpolated values of K_a,[9] K_b[10] and K_w.[11] Results for the NH_3–HOCl reaction are shown in Table IV and for the methylamine and dimethylamine reactions in Table VII. Figure 2 shows plots of the logarithms of the specific rate constants against the reciprocal of the absolute temperature. The activation energies and other reaction terms are shown in Table IX.

TABLE IX

KINETIC FACTORS FOR CHLORAMINE FORMATION

Chloramine	Specific rate constant (25°) (non-ionic)	Specific rate constant (25°) (ionic)	E_{act}	Arrhenius factor, A (non-ionic)
NH_2Cl	3.7×10^8	5.6×10^6	2500	2.5×10^{10}
CH_3NHCl	3.0×10^{10}	19.3×10^6	4500	6.0×10^{13}
$(CH_3)_2NCl$	3.0×10^{10}	13.7×10^6	800	1.2×10^{11}

The accuracy of the results in basic solution is limited by the accuracy with which the ionization constant of HOCl is known as a function of temperature. However, since the same set of K_a values is used for all three reaction systems, the relative magnitudes of the activation energies are not affected by errors in K_a. In addition, the agreement of the activation energy obtained in acid solution for the NH_3–HOCl system with that in basic solution indicates an accuracy of ±1 kcal.

The Mechanism of the Reaction.—It has been shown by equations (9–14) that it is impossible to distinguish between the ionic and non-ionic mechanisms for these reactions through salt effects. The same equations indicate that it will be very difficult, if not impossible, to distinguish the mechanisms by any other kinetic effect, for no approximations have been made in deriving the expression which shows that the kinetic behavior according to either mechanism should be exactly the same. Even changing the dielectric constant or the solvent will be ineffective so long as the activity coefficients are reduced to a common base and the change in ionization constants is taken into account.

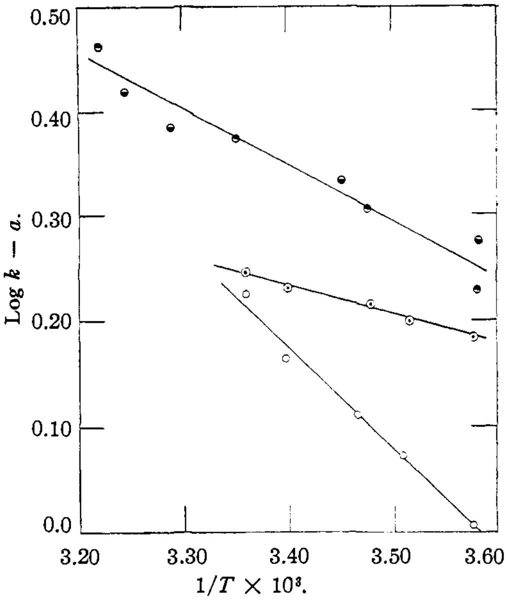


Fig. 2.—The temperature dependence of the specific rate constants for monochloramine formation. The constant *a* is used to space the lines conveniently: NH_3–HOCl reaction, $a = 8.170$, ◓ *p*H–4.58, ◒ $[OH^-] = 5.3 \times 10^{-3}$; CH_3NH_2–HOCl reaction, $a = 10.250$, ○ $[OH^-] = 0.12$; $(CH_3)_2NH$–HOCl reaction, $a = 10.230$, ⊙ $[OH^-] = 0.12$.

The statistical approach to reaction kinetics indicates that the question of these alternative mechanisms may be a meaningless one. If the situation resembles that shown diagrammatically in Fig. 3a, then the rate must be exactly the same whether the reaction path goes directly from the ions to the activated complex or by way of the neutral molecules. The postulated equilibrium between reactants and activated complex must be independent of the path, and so the resultant concentration of activated complex must result from a combination of both paths.

The question of mechanism becomes significant if the configuration of the activated complex is such that it is difficult to attain it from one of the proposed sets of reactants. This is equivalent to saying that the alternative mechanisms have different activated states. Such a situation is pictured in Fig. 3b, which portrays an instance in which there is a configurational or energy barrier for the ionic reactants. Since the activated state for the ionic mechanism has a higher free energy than the normal activated complex, the reaction will, for the most part, proceed by way of

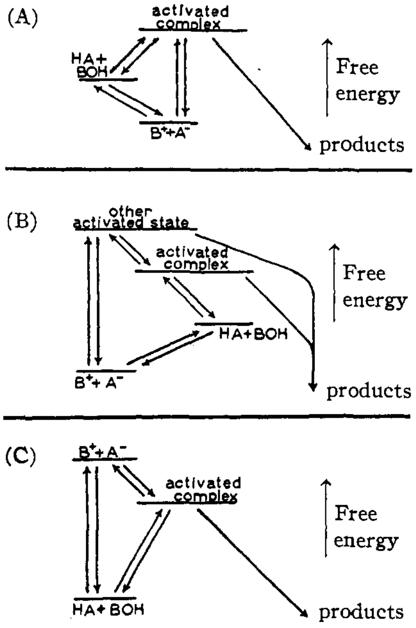


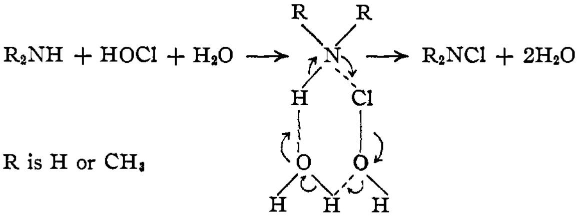
Fig. 3.—Free energy relationships of possible ionic and non-ionic reaction mechanisms.

the non-ionized molecules. Naturally the roles of non-ionized and ionized reactants in this picture might be reversed. Even for this case kinetic studies will give no information as to which reactants are playing which roles.

Figure 3c depicts the situation which seems to be the only one leading to a definite conclusion. If the free energy of one of the possible sets of reactants lies higher than the free energy of the activated complex, then the reactants will certainly be those substances at the lower free energy level. Such a condition might result by working in solvents in which free energy of solvation did not stabilize the ions. Whether such a situation is experimentally obtainable for the present reactions is not known.

The reactions of ammonia and the methylamines with hypochlorous acid appear to be similar to Fig. 3b, since it is relatively easy to imagine configurations for an activated complex which can be formed readily from the free base and HOCl by utilizing the free electron pair on the nitrogen atom, whereas it is considerably more difficult to suggest plausible complexes for the NH_4^+ or methylammonium ions and OCl^-.

If the free electron pair on the nitrogen is directly involved in the formation of the activated complex, the reaction is similar to an S_N2 reaction or nucleophilic displacement and the rates of reaction should vary as the base strength of the nitrogen compound. They are, in fact, approximately proportional, since the ratios of the specific rate constants to the basic ionization constants at 25° are 2.2, 7.1 and 5.0×10^{13} for ammonia, methylamine and dimethylamine, respectively. However, it is not likely that these nitrogen bases will displace the stronger hydroxyl group from the HOCl molecule unless neutralization of the hydroxyl occurs simultaneously. Hence, a cyclic transition state is postulated in which combination of the hydrogen and hydroxyl proceeds at the same time as the displacement. The whole process, therefore, is one concerted action consummated by an electron shift. In the following diagram, which depicts the proposed mechanism, a molecule of water has been included in the activated complex because it allows a more stable cyclic configuration.[13] Whether or not this is part of the complex can only be checked by experiments in other solvents.



If the reactants are the ions, a different reaction path seems probable since the ammonium or substituted ammonium ions have no free electron pairs for interaction with the chlorine of the OCl^- ion. One therefore expects a substitution mechanism, which should occur most readily with the ammonium ion, since it has the greatest number of available hydrogens and the nitrogen atom is less shielded from the action of the chlorine by attached groups. The relative magnitudes of the specific rate constants for the ionic mechanism in Table IX shows that this prediction is not in accord with the data. Consequently, the molecular mechanism seems more likely.

The Ammonium Cyanate Reaction.—A reaction with many similarities to those discussed here is the formation of urea from ammonium cyanate, which has been kinetically investigated in a very thorough manner.[14,15,16] The reaction has generally been interpreted as occurring by an ionic mechanism according to the equation

$$NH_4^+ + OCN^- \longrightarrow (NH_2)_2CO$$

However, equation (14), developed for the NH_3–HOCl reaction, is equally applicable to the present case since HOCN is also a weak acid.[17] Consequently, the effects of ionic and dielectric strength, which have been used to classify the ammonium cyanate reaction as typically ionic, are equally consistent with the non-ionic mechanism

$$NH_3 + HOCN \longrightarrow (NH_2)_2CO$$

Further, as in the case of the NH_3–HOCl reaction, it appears easier to visualize a reaction path for

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[13] It is also quite probable that more than one molecule of water is present in the complex.

[14] Walker and Hambly, *Trans. Chem. Soc.*, **67**, 746 (1895).

[15] Warner and Stitt, This Journal, **55**, 4807 (1933).

[16] Warner and Warrick, *ibid.*, **57**, 1491 (1935).

[17] $K_a = 1.2 \times 10^{-4}$ (0°), Heilbron, "Dictionary of Organic Compounds," Eyre and Spottiswoode, Ltd., 1943, Vol. 1, p. 585.

the non-ionic mechanism than for the ionic mechanism. It is apparent that the evidence for the ionic nature of this and similar reactions needs careful re-examination.

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Summary

The rates of formation of NH_2Cl, CH_3NHCl and $(CH_3)_2NCl$ from HOCl and the appropriate amine have been studied in dilute aqueous solution under a variety of experimental conditions. The reactions are second order with respect to concentrations of the reactants, but the rates show a marked dependence on the *p*H of the solution.

The observed variations in rates with *p*H can be quantitatively accounted for by considering that reaction occurs either between HOCl and NH_3, CH_3NH_2 or $(CH_3)_2NH$, or between OCl^- and NH_4^+, $CH_3NH_3^+$ or $(CH_3)_2NH_2^+$.

It has been shown mathematically that for reactions of this type, between weakly ionized substances, it is impossible to distinguish kinetically between the mechanism which assumes ions to be the reactants and that which assumes molecules to be the reactants. On this basis the validity of the evidence for the ionic nature of the ammonium cyanate reaction has been questioned.

Evidence has been presented which indicates that the molecular mechanism is more probable for the formation of the chloramines. On this basis the rates of the reactions can be expressed by the equations

$$d[NH_2Cl]/dt = 2.5 \times 10^{10}e^{-2500/RT}\ [NH_3][HOCl]$$

$$d[CH_3NHCl]/dt = 6.0 \times 10^{13}e^{-4500/RT}[CH_3NH_2][HOCl]$$

$$d[(CH_3)_2NCl]/dt = 1.2 \times 10^{11}e^{-800/RT}[(CH_3)_2NH][HOCl]$$

CAMBRIDGE, MASSACHUSETTS SEPTEMBER 29, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Electric Polarization of Carboxylic Acids. III. A Study of the Association of Some Additional Carboxylic Acids in Benzene Solution[1]

BY ARTHUR A. MARYOTT,[2] MARCUS E. HOBBS AND PAUL M. GROSS

The association of carboxylic acids in hydrocarbon and certain other organic solvents as well as in the vapor phase has been the subject of numerous investigations by a variety of methods. With regard to association in solution, however, relatively few reliable quantitative data are available. Exceptions are the isopiestic measurements of Wall and co-workers[3,4] on benzoic acid and several other non-volatile acids in benzene. Although the more generally applicable methods involving distribution between water and an immiscible organic solvent has been used on occasion, this procedure is open to question because of the effect of the finite solubility of the water on the association equilibrium in the second medium.[5,6]

In earlier papers from this Laboratory,[7,8] it was shown that measurements of the dielectric constants of very dilute solutions of carboxylic acids in the non-polar solvents, benzene and heptane, could be used to study the association of these acids. Assuming that only monomeric and dimeric forms were present at these low concentrations, the data permitted evaluation of the dimer–monomer equilibrium constants as well as the polarizations of the monomeric and dimeric forms. The dipole moments obtained for the monomer were in reasonable agreement with values reported in dioxane where the acids do not associate. In all cases the polarization of the dimer was found to be from 17 to 26 cc. greater than would be expected in view of recent electron diffraction studies[9] which indicated a planar symmetrical structure. Evidence was presented, in particular from measurements on the three monofluorobenzoic acids,[8] in support of the planar configuration, and it was concluded that the anomalous polarization of the dimer was due to an exceptionally high atomic polarization rather than to any dipolar contribution.

In the present investigation, the dielectric constants of dilute benzene solutions of seven additional acids have been measured. These include *o*-toluic, *m*-toluic, cinnamic (*trans*), crotonic (*trans*), phenylacetic, *β*-phenylpropionic and stearic acids. These together with acids previously studied afford a sufficient series to determine whether any systematic correlation exists between the structure of the acid and its tendency to associate.

Experimental

Materials.—Reagent grade, thiophene-free benzene was stored over phosphorus pentoxide for several weeks and

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[1] The contents of this paper were presented at the St. Louis meeting of the American Chemical Society, March, 1941.

[2] Ethyl Dow Post-Doctorate fellow, 1941. Present address: National Bureau of Standards, Washington, D. C.

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[8] A. A. Maryott, M. E. Hobbs and P. M. Gross, *ibid.*, **9**, 415 (1941).

[9] L. Pauling and L. O. Brockway, *Proc. Natl. Acad. Sci.*, **20**, 336 (1934); J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).