816. *Kinetics of the Reaction Between Chloramine and Tertiary Amines.*

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The rate of the reaction of chloramine with several tertiary amines has been studied in a variety of solvents. The reaction of tri-n-alkylamines with chloramine is faster than that with alkyl halides, but is similar in many other respects. All follow second-order kinetics in organic solvents, decrease in rate with increasing amine chain length, and are greatly affected by the solvent. Two possible reaction mechanisms are discussed.

Omietanski and Sisler[1] reported that reaction of chloramine with a variety of tertiary amines affords 1,1,1-trisubstituted hydrazinium chlorides: $R_3N + NH_2Cl \longrightarrow [R_3N{\cdot}NH_2]^+Cl^-$.

Hydrazinium chlorides are in many respects similar to the corresponding quaternary ammonium chlorides, obtained by the reaction of tertiary amines with alkyl or aryl chlorides: $R_3N + R'Cl \longrightarrow [NR_3R']^+Cl^-$. In organic solvents, the reaction of straight-chain tertiary amines with alkyl halides follows second-order kinetics. It is, in fact, one of the typical examples of a reaction pursuing the bimolecular mechanism, described extensively in the literature.

As part of our work on the reactivity of chloramine with certain tertiary amines, kinetics of these systems were determined. This provided an opportunity for comparing both the order and the rate constant of the two reactions. A further object was to evaluate the effect of different solvents and of amine chain length.

Experimental

Chloramine Solutions.—Chloramine, an unstable gas, cannot be used in pure form for kinetic measurements. Previous studies[2] had not clearly shown whether solutions of chloramine could be prepared which would be sufficiently stable for quantitative kinetic measurements.

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[1] Omietanski and Sisler, *J. Amer. Chem. Soc.*, 1954, **79**, 121.

[2] Marckwald and Willie, *Ber.*, 1923, **56**, 1319; Corbett, *J.*, 1953, 1927; Chapin, *J. Amer. Chem. Soc.*, 1929, **51**, 2112; Audrieth and Rowe, *ibid.*, 1955, **77**, 4726.

The preparation, stability, and handling properties of chloramine in a variety of solvents were therefore investigated.

A gaseous mixture of chloramine and an excess of ammonia, produced by the method of Sisler *et al.*,[3] was bubbled into the solvent selected. Chloramine was absorbed by the solvent (ether or benzene); its concentration was determined in the solution by iodimetric titration. This procedure was considered preferable to the conventional method of extracting hypochlorite–ammonia solutions, as it avoided the risk of having hypochlorite present instead of chloramine.

For preparing chloramine solutions in solvents which absorb excessive quantities of ammonia, an 0·5M-solution of chloramine in benzene was made as described, and extracted immediately with one-tenth of its volume of water to remove the excess of ammonia and suspended ammonium chloride. A second extraction with 1—4 times its volume of water resulted in the formation of chloramine–water solutions of the desired concentration range.

These water solutions, if used rapidly, were also suitable for preparing chloramine solutions in hexane, chloroform, and carbon tetrachloride by simple extraction.

Chloramine–alcohol solutions could not be prepared by either of these methods. As only low chloramine concentrations were required, a small amount of 1—2M-chloramine–ether solution was added to the alcohol. The ether content of the final solution was less than 5% in all instances.

To compare the stability of the different solutions, samples were stored at 25° ± 0·05°, and their chloramine contents determined periodically by iodimetric titration. Fig. 1 shows the results of a series of these determinations.

Chloramine–ether solutions are exceptionally stable. Samples were in many instances kept for several weeks with only 1—2% of decomposition. At equal starting concentration, other solutions decompose more or less rapidly, depending on the nature of the solvent.

Amines.—Pure grades of commercially available trimethylamine, triethylamine, and " dimethylperhydrotallowamine " were used after further purification by conventional means. " Dimethylperhydrotallowamine " is a commercial ~2 : 1 mixture of dimethyl-octadecylamine and -hexadecylamine.

Experimental Procedure and Analyses.—The following general procedure was used for determining the rate of reaction of chloramine with tertiary amines. A chloramine solution in the solvent was adjusted to the desired concentration, which was checked by titration immediately before use. Another solution, stored at 25°, contained the calculated quantity of the tertiary amine. Both solutions were then combined in a round-bottomed, three-necked flask equipped with a stirrer and an internal thermometer, and immersed in a water-bath controlled thermostatically at 25° ± 0·05°. Zero time was taken at the instant the solutions were mixed.

Samples were then withdrawn with a pipette provided with a glass-wool filter at the tip to prevent clogging by deposited hydrazinium or ammonium chloride. More concentrated solutions were sampled with a large-bore pipette for the same reason. Pipettes were then emptied rapidly into an acidified potassium iodide solution and titrated with 0·1 or 0·02N-sodium thiosulphate.

This iodimetric titration procedure was found to be very satisfactory for these determinations The more elegant spectrophotometric method [4] could not be used because of the turbidity caused by the solid hydrazinium chloride.

The concentrations of hydrazinium chloride, amine hydrochloride, and ammonium chloride were determined at the end of the reaction (48 hr. in most cases). For this purpose, smaller separate samples were kept at 25°, and then analysed in the following way:

The solvent was evaporated at 60°, and the dry salts were taken up in anhydrous chloroform. Any ammonium chloride present remained undissolved. It was filtered off, washed with more chloroform, dissolved in water, and titrated with 0·1N-silver nitrate. Amine hydrochloride was converted into free amine and ammonium chloride by bubbling gaseous ammonia through this chloroform solution. The solution was filtered again, if necessary (amine hydrochloride is rarely present). The remaining chloroform filtrate contained the hydrazinium chloride, which was determined by argentometric titration as the chloride.

In exploratory experiments, kinetic measurements were made at an equal initial concentration of 0·2 mole/l. of triethylamine and chloramine. Plotting the reciprocal values of the

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[3] Sisler, Neth, Drago, and Yaney, *J. Amer. Chem. Soc.*, 1954, **76**, 3906.

[4] Kleinberg, Tecotsky, and Audrieth, *Analyt. Chem.*, 1954, **26**, 1388.

residual chloramine concentration against time gave a straight line for all the organic solvents: *i.e.*, rate constants, k_2, remained constant with time. This was not true when water was the solvent, as shown in Table 1.

TABLE 1. *Reaction of trialkylamines with chloramine in water.*[a]

Trimethylamine			*Triethylamine*		
Time (sec.)	Chloramine reacted (%)	Rate constant, k_2 (l. mole^{-1} sec.$^{-1}$)	Time (sec.)	Chloramine reacted (%)	Rate constant, k_2 (l. mole^{-1} sec.$^{-1}$)
0	0	—	0	0	—
60	48·1	0·157	75	24·1	0·0427
269	76·0	0·107	300	46·3	0·0244
419	82·3	0·099	435	54·2	0·0229
660	85·0	0·042	643	61·6	0·0202
1920	90·1	0·022	2340	74·2	0·0073

[a] At equal chloramine and amine starting concentrations of 0·1 mole/l.

Hydrazinium chloride was found, as expected, on complete analysis of the products from triethylamine and chloramine in ether; however, ~10% of ammonium chloride was also present.

Interference by Ammonia.—It is known, that ammonium chloride is formed in the decomposition of chloramine. However, 0·2M-chloramine solutions in ether do not give precipitates of ammonium chloride in 48 hr. One must assume that the presence of tertiary amine favoured the decomposition of chloramine or its reaction with any ammonia present. To check this hypothesis, parallel experiments were run: in one sample the ammonia concentration in ether was increased by 0·12 mole/l. by saturation at low temperature. A second solution was prepared in the conventional manner and used as a control. A complete analysis after 48 hr. at 25° ± 0·05° gave the results shown in Table 2.

TABLE 2. *Effect of ammonia content on ammonium chloride formation in ether.*[a]

Initial concn. of NH_3 (N)	0·1	0·22
$[Et_3N{\cdot}NH_2]Cl$ (mole %)	91	73
NH_4Cl (mole %)	9	27

[a] Starting concentration of chloramine and tertiary amine 0·2 mole/l.

It is evident that higher concentrations of ammonia in the reaction solution result in formation of more ammonium chloride, *i.e.*, ammonia competes with the tertiary amine for the chloramine present.

Ammonia can be removed by treating the chloramine solutions with cadmium or copper salts. However, the resulting solutions were not as stable to decomposition as before, possibly owing to formation of dichloramine at a lower pH.

The following alternative method was tried and found to be satisfactory: Dilute solutions of chloramine in ether, benzene, or alcohol were treated with a 16—20 molar excess of the tertiary amine at 25°. After 48 hr., samples were analysed and found to contain only hydrazinium chloride. This procedure was used for all further kinetic work. It required more dilute solutions of chloramine, usually 0·005—0·05 mole/l., as rates would otherwise be too rapid for effective measurement.

Ionic-strength Effects.—Hydrazinium salts formed in the reaction are very soluble in water, soluble in alcohols or carbon tetrachloride, and nearly insoluble in ether, benzene, or hexane. It is known that changes in the ionic strength or surface effects of precipitated salts could influence the reaction rates in solvents. To ascertain the magnitude of such changes, experiments were made with chloramine and triethylamine in ether and in methanol, to which a large excess (100 times the amount expected after complete reaction) of triethylhydrazinium chloride was added before the reaction. Control runs without this excess were carried out simultaneously.

Methanol was used to evaluate the effect on the rate constant under the worst possible conditions, as much of the excess of hydrazinium salt added dissolved in this system. The second-order rate constants, k_2, for these two runs were: $4{\cdot}25 \times 10^{-3}$ for the control and $5{\cdot}33 \times$

10^{-3} l. mole^{-1} sec.$^{-1}$ for the run with excess of hydrazinium chloride. As expected, an ionic salt accelerates the rate of this type of reaction, but the increase is small in view of the large excess used.

Rates in ether, which is a poor solvent for hydrazinium chlorides, were not affected by the addition of this salt. Under these circumstances, the effect of ionic-strength changes or precipitated salt can be considered negligible at ordinary concentrations, especially in non-polar solvents.

Use of Excess of Amine.—Fig. 2 shows the reaction of an excess of trimethylamine, triethylamine, and " dimethylperhydrotallowamine " with chloramine in ether. The straight lines obtained indicate that all reactions were of the second order. The slope of the lines is equal to the rate constant (k_2) in l. mole^{-1} sec.$^{-1}$. Individual k_2 values, calculated at different conversions up to 75%, did not vary by more than 6% in a single determination.

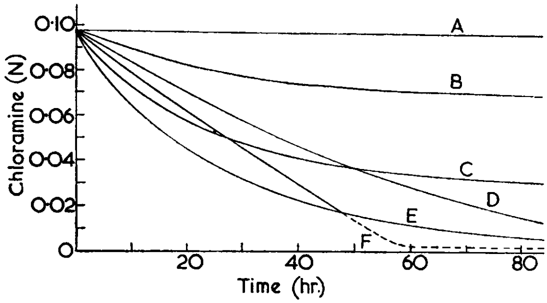


FIG. 1. *Stability of chloramine solutions at* 25°.

A, *Ether.* B, *Benzene.* C, *Carbon tetrachloride.* D, *Propan-2-ol.* E, *Hexane.* F, *Methanol.*

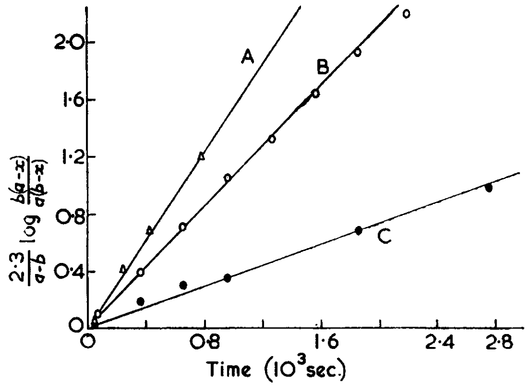


FIG. 2. *Reaction of trialkylamine with chloramine in ether.*

A, *Trimethylamine.* B, " *Dimethylperhydrotallowamine.*" C, *Triethylamine.*

DISCUSSION

Reaction rate constants for triethylamine and chloramine in various solvents are shown in Table 3.

TABLE 3. *Rate constants* (l. mole^{-1} sec.$^{-1}$) *for the reaction between triethylamine and chloramine at* 25°.[a]

Solvent:	Et_2O	C_6H_{14}	MeOH	C_6H_6	CCl_4	H_2O
10^4k_2	3·7	5·4	42·5	65·0	74·0	(200—300 [b])

[a] Amine present in 16—20 molar excess. [b] Accurate values are not available as k_2 decreases with time. This Table shows the general trend towards faster rates with increasing polarity of the solvent. It is interesting that the reactions are slowest in ether, the solvent in which chloramine is also unusually stable. Internal bonding or solvation effects of the type $(Et_2O{\cdot}NH_2)Cl$ could possibly be involved here. The same may apply to the reaction rates in methanol, which are slower than in benzene.

Previous workers[5] have also studied the effect of changes in length of the alkyl group of tertiary amines on the reaction rate with alkyl halides. A substantially slower reaction was reported with increasing size of the substituent group for all simple tertiary amines, caused mainly by steric hindrance. The rates obtained in our study for the reaction of chloramine with tertiary alkyl amines are shown in Table 4.

TABLE 4. *Rate constants* (k_2 *in* 10^4 l. mole^{-1} sec.$^{-1}$) *for the reaction of tertiary amines with chloramine at* 25°.

	NMe_3	" Dimethylperhydro-tallowamine "[a]	NEt_3
In ether	15·5	(10·7)	3·7
In benzene	623	(476[b])	65

[a] These values are only qualitative and represent the reaction of a mixture of alkyldimethylamines with chloramine. Kinetics were, however, strictly of the second order. [b] At equimolar concentration (0·1N) of chloramine and amine. All others with a 16 : 1 molar excess of amine.

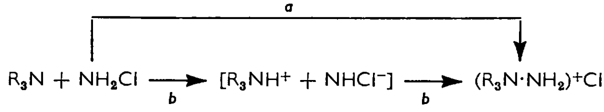
Differences between the amines are not quite as large as were reported for alkylation to quaternary ammonium chlorides, though the trend is the same: comparison is shown in Table 5. It is evident that the chloramination of amines is remarkably rapid.

TABLE 5. *Rates of reaction* (10^4k_2 *in* l. mole^{-1} sec.$^{-1}$) *of tertiary amines in benzene.*

	Chloramine	MeI	EtI
Trimethylamine	623	185[a]	2·1[a]
Triethylamine	65	15·4[a]	(3·5)[b, c]

[a] Winkler and Hinshelwood, *J.*, 1935, 1147. [b] Moelwyn-Hughes and Hinshelwood, *J.*, 1932, 233. [c] At 100°; all other at 25°.

Reaction Mechanism.—The reaction of chloramine with tertiary amines proceeds in all probability by either of the two following mechanisms:



Mechanism *a*, proposed by Omietanski and Sisler,[1] is a bimolecular displacement. Our studies indicate that the kinetics of the reaction of chloramine with tertiary amines in organic solvents are definitely of the second order as required for concept *a*.

Our results also show that addition of a tertiary amine to a stable solution of chloramine in ether containing some ammonia gave hydrazinium chloride and ammonium chloride simultaneously. The reaction (decrease in chloramine content) nevertheless followed strict second-order kinetics in organic solvents.

These observations can be explained if we assume that the two reactions are simultaneous and of the second order. According to the concepts of Cahn and Powell,[6] a proton acceptor is required for the formation of ammonium chloride. This would explain the formation of ammonium chloride when triethylamine is added to a stable chloramine–ether solution.

Mechanism *b* is a modified version of that postulated by Audrieth *et al.*[7] for the reaction of chloramine with ammonia or primary or secondary amines. It involves the intermediate formation of a chloramide ion, resulting from the action of a strong proton acceptor such as a tertiary amine on chloramine. This chloramide ion, once formed, could

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[5] Zaki and Fahim, *J.*, 1942, 270.

[6] Cahn and Powell, *J. Amer. Chem. Soc.*, 1954, **76**, 2565, postulate the intermediate formation of a hydrazinium salt $(NH_3{\cdot}NH_2)Cl$ from chloramine and ammonia. Free hydrazine is then produced by the action of base on this intermediate. In presence of an excess of chloramine, hydrazine then reacts to form ammonium chloride and nitrogen.

[7] Audrieth, Colton, and Jones, *J. Amer. Chem. Soc.*, 1954, **76**, 1428.

then react to give a hydrazinium chloride with the tertiary amine or it may undergo ultimate conversion into ammonium chloride with ammonia. Since a strong base is required for initiation of the reaction according to this concept, chloramine as such should not (or at least not rapidly) react with ammonia in solution in absence of a tertiary amine or some other proton acceptor.

Although the mechanism by Omietanski and Sisler appears to be the simpler one, both concepts explain the present results in organic solvents. Additional work would be required to clarify these problems.

In the limited number of runs carried out with chloramine and a tertiary amine in water, the results do not seem to follow second-order kinetics. It is possible that reactions in this solvent do not proceed as indicated but are more complicated and require further study.

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