[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Kinetics of the Ammonolysis of 2-Chlorobenzothiazole by Liquid Ammonia

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With but few exceptions, studies of ammonolytic reactions have been of a qualitative character.[1] Quantitative investigations have been concerned entirely with the ammonolysis of ester-type linkages.[2–8] A quantitative study of the ammonolysis of 2-chlorobenzothiazole[9] (an ammonolytic reaction involving a carbon–halogen bond) is reported in the present paper.

Experimental

Materials.—2-Chlorobenzothiazole,[10] anhydrous ammonia[11] and ammonium benzoate[12] were prepared and purified as described in the literature. Reagent grade ammonium chloride, sodium chloride, and potassium chloride were recrystallized several times from water and dried thoroughly.

Identification of the Ammonolysis Products.—The products from a completed reaction between 2-chlorobenzothiazole and liquid ammonia (in a sealed tube at 30°) were washed with water. The water-insoluble product was recrystallized from benzene giving a quantitative yield of 2-aminobenzothiazole, m. p. 127–128°. A mixture with an authentic specimen of 2-aminobenzothiazole (m. p., 125–127°) melted at 126.5–128°. The water-soluble portion gave positive tests for ammonium and chloride ions.

Attempted Hydrolysis of 2-Chlorobenzothiazole.—Samples of 2-chlorobenzothiazole were not hydrolyzed when agitated with water at room temperature for four weeks or when refluxed for ten hours. In both cases, the aqueous layer failed to give a positive test (with silver nitrate) for chloride ion.

Procedure.—From special burets calibrated to deliver 0.5 or 1 g. samples, 2-chlorobenzothiazole was delivered into Pyrex tubes (1.5 × 30 cm.) which were calibrated to contain 10 ml. For reactions involving an added salt, a known weight of the salt was introduced before introduction of the thiazole. Anhydrous ammonia was condensed to the 10-ml. calibration mark, the tube was sealed and allowed to warm to room temperature. The contents were mixed and the tube placed immediately in a thermostat maintained at 30 (or 20) ± 0.1°. The time of mixing, to the nearest minute, was taken as the starting time of the reaction At known intervals of time, tubes were removed, immediately cooled in an acetone–dry-ice mixture, and opened. The open end of each tube was drawn to a fine capillary, and the ammonia allowed to vaporize. Residual ammonia was removed by evacuation. (Reaction occurring subsequent to removal from the thermostat was assumed to be negligible.) The reaction products were extracted twice with mixtures of ether and water; the aqueous layers were separated, combined, made up to a known volume, and analyzed for chloride ion by a modified Volhard procedure.[13]

Data.—A typical set of experimental data (relating to a reaction at 30° involving 1.0 g. of C_7H_4ClNS in a total volume of 11.9 ml. of solution) is given in Table I. Data on reactions involving excess liquid ammonia and 0.5 g. (42.0 mg. of C_7H_4ClNS/ml.), 1.0 g. (84.0 mg./ml.), and 2.0 g. (168.9 mg./ml.) samples of 2-chlorobenzothiazole are summarized graphically in Fig. 1.

TABLE I

AMMONOLYSIS OF 2-CHLOROBENZOTHIAZOLE

Time, hr.	8.0	18.0	24.0	34.5	40.0	48.0	56.0
$[Cl^-]$, mg./ml.	2.44	4.69	5.57	6.84	7.13	7.69	8.00

For the above concentrations the total volumes of solution at 30° were 11.9, 11.9 and 11.8 ml., respectively. Data for reaction in the presence of added salts are summarized in Table III. Each item of data represents the average of two closely-agreeing experimental measurements.

The Action of Potassium Amide on 2-Chlorobenzothiazole.—2-Aminobenzothiazole could not be isolated from the products of a reaction between 7.56 g. of 2-chlorobenzothiazole and the potassium amide from 1.76 g. of potassium in 30 ml. of anhydrous liquid ammonia in a Faraday tube[14] at 0°. The reaction was markedly exothermic and resulted in the formation of a tan-colored solid and a dark brown solution. There were isolated two solid products which were not identified.

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[1] For review and primary references see Fernelius and Bowman, *Chem. Rev.*, **26**, 3–48 (1940).

[2] Shatenshtein, *et al.*, *Acta Physicochim.* (U. S. S. R.), **3**, 37 (1935).

[3] Shatenshtein, *ibid.*, **5**, 841 (1936); *J. Phys. Chem.* (U. S. S. R.), **8**, 696 (1936); THIS JOURNAL, **59**, 432 (1937).

[4] Markova and Shatenshtein, *Acta Physicochim.* (U. S. S. R.), **11**, 117 (1939).

[5] Shatenshtein and Markova, *ibid.*, **11**, 131 (1939).

[6] Slobutsky and Audrieth, *Trans. Illinois State Acad. Sci.*, **29**, 104 (1936).

[7] Slobutsky, Audrieth and Campbell, *Proc. Nat. Acad. Sci.*, **23**, 611 (1937).

[8] Fellinger and Audrieth, THIS JOURNAL, **60**, 579 (1938).

[9] Watt, *J. Org. Chem.*, **4**, 437 (1939).

[10] Scott and Watt, *ibid.*, **2**, 148 (1937).

[11] Johnson and Fernelius, *J. Chem. Education*, **6**, 441–444 (1929).

[12] McMaster, *Am. Chem. J.*, **49**, 294 (1913).

[13] Caldwell and Moyer, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 38 (1935).

[14] For experimental details see Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., pp. 317–330; Johnson and Fernelius, *J. Chem. Education*, **6**, 447 (1929).

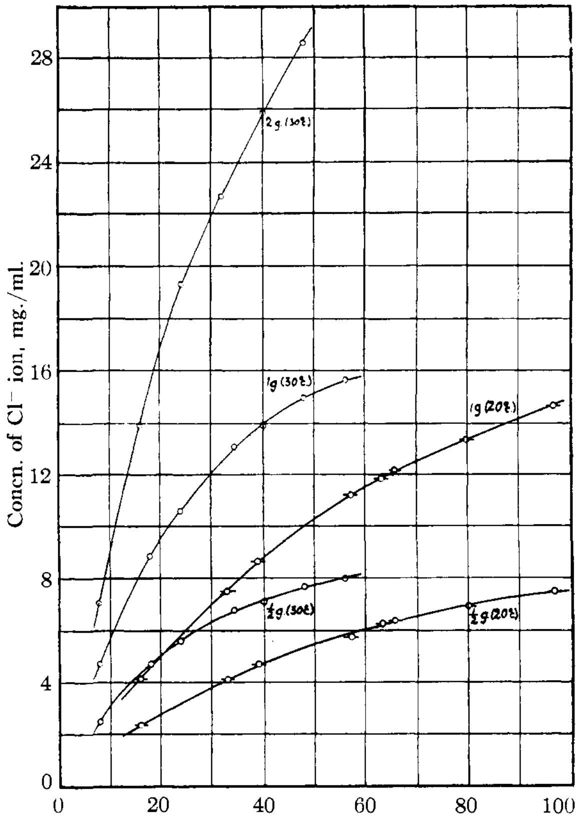
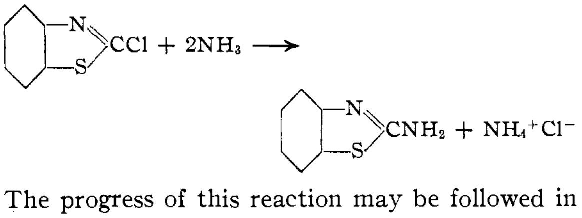


Fig. 1.

Discussion

The ammonolysis of 2-chlorobenzothiazole involves the reaction



The progress of this reaction may be followed in terms of the halide ion produced since it has been shown that 2-chlorobenzothiazole is not appreciably hydrolyzed.

Velocity Constants.—Since ammonia was present in large excess, it was assumed that the change in its concentration during the course of a rate determination was negligible. The slight differences in the total volume of solution at different temperatures were also neglected since the resulting variations were within the range of experimental error. Values of log $(a - x)$, (where a = initial concentration of C_7H_4ClNS in mg./ml., and x = number of mg. of C_7H_4ClNS/ml. reacting in time t) were calculated from the experimental data and plotted *versus* time (Fig. 2). The straight lines obtained indicate that the ammonolysis is a pseudo-unimolecular reaction, for which

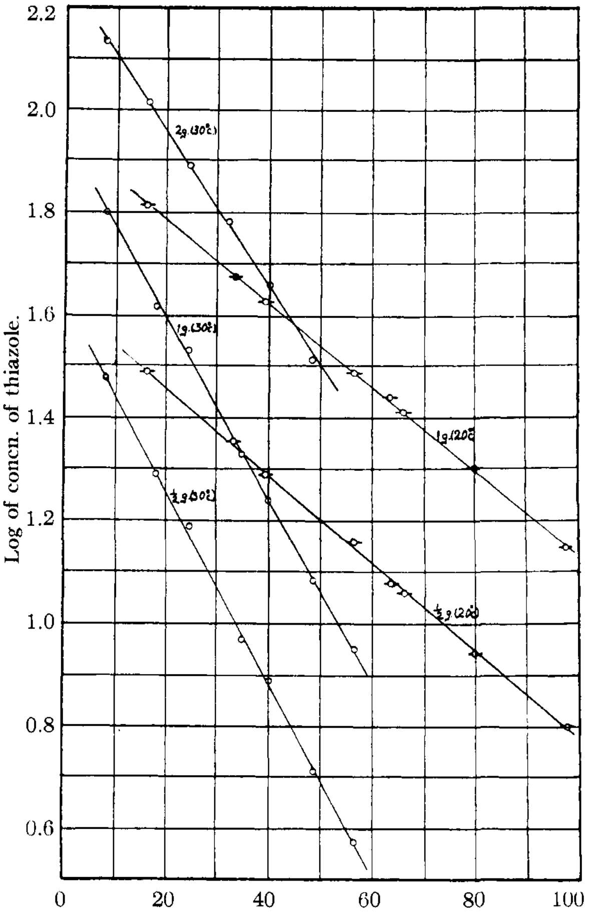


Fig. 2.

$$-\log(a - x) = (k/2.303)t + \text{const.}$$

Values for the velocity constant k were determined from the slopes of the lines. (Two completely independent rate measurements gave values which checked within 1%.) The velocity constants are summarized in Table II.

TABLE II

REACTION VELOCITY CONSTANTS

Initial concn. of C_7H_4ClNS, mg./ml.	Temp., °C.	Velocity const., hr.$^{-1}$
42.0	20	0.0198
84.0	20	.0186
42.0	30	.0430
84.0	30	.0405
168.9	30	.0354

Energy of Activation.—The temperature coefficient (k_{303}/k_{293}) was obtained from the rate measurements at 20 and 30°. For samples having initial concentrations of 42.0 and 84.0 mg./ml., the temperature coefficients were found to be 2.172 and 2.178, respectively. The values for the energy of activation (E) calculated from these data were 13,680 and 13,730 cal./mole. In consideration of the average deviation in temperature ($\pm 0.1°$), and the experimental error in the values of the velocity constant (approximately 1%), the *maximum* possible error (in E) should be of the order of ±700 cal./mole.

Mechanism of Reaction.—Since a pseudo-unimolecular reaction is indicated, the most probable mechanism would involve a bi-molecular reaction of molecules of the thiazole and ammonia as the rate-determining step. That the rate of reaction is actually dependent upon the concentration of ammonia is shown in Table II. Since each sample was prepared by adding sufficient liquid ammonia to provide the same final volume, variation in the concentration of thiazole also produced change in the concentration of ammonia. The latter variations are reflected in the corresponding values of the reaction velocity constants.[15]

The rate equation for the reaction was concluded to be

$$-\,d[C_7H_4ClNS]/dt = k[C_7H_4ClNS][NH_3]$$

The possibility of a bimolecular reaction involving the amide ion appears to be eliminated in view of the effect of added ammonium chloride (see Table III). The ion-product constant for liquid ammonia[16] (at −34°) is 5×10^{-34}. In the presence of 0.314 M ammonium chloride, the concentration of the amide ion should be decreased by a factor of 10^{-16}; yet the rate of reaction is found to be increased by 7%. While study of the reaction between 2-chlorobenzothiazole and potassium amide did not lead to conclusive results, it was shown that the reaction in the presence of a high concentration of amide ion is not one of simple ammonolysis.

A third possibility is that the rate-determining step is actually a true unimolecular decomposition of a thiazole-ammonia complex. There is, however, at present no evidence for the existence of any such complex as a real component of the solution.

Influence of Salts.—From the experimental data on the rate of the reaction in the presence of added salts, the velocity constants were determined. In Table III are listed the velocity constants, and the ratios of the velocity constant (k_1) for reaction in the presence of each salt to the constant (k) for reaction in the absence of any added salt. In every case, the results indicate a pseudo-unimolecular reaction, and there is no evidence of pronounced specific catalytic activity on the part of any of the ions added.

The results obtained by other investigators[2–8] on the ammonolysis of santonin, pilocarpine, diethyl malonate, and ethyl benzoate show that these reactions are markedly catalyzed by salts which behave as acids in liquid ammonia. Although direct comparison with each of these cases is not possible, it is notable that the effects of salts such as ammonium chloride and ammonium benzoate upon the ammonolysis of 2-chlorobenzothiazole are far less than their effects upon the ammonolysis of esters. It should be noted also that the neutral salt, sodium chloride, apparently has slightly more effect upon the ammonolysis of the thiazole than does the acid, ammonium chloride.

TABLE III

INFLUENCE OF ADDED SALTS

Salt	[a]Concn. of salt, mg./ml.	Velocity constant	k_1/k
None	. . .	0.0405	1.00
KCl	23.42	.0410	1.01
NaCl	18.36	.0446	1.10
NH_4Cl	16.81	.0432	1.07
$NH_4O_2CC_6H_5$	43.69	.0431	1.06

[a] In each case the concentration of salt was 0.314 M. The initial concentration of thiazole was 84.0 mg./ml., the total volume of solution was 11.90 ml. and the temperature was 30°.

Additional experimental evidence is necessary to make possible a broad comparison of the ammonolysis of organic halides and esters, and to elucidate the character of the effects produced (upon ammonolytic reactions in general) by neutral salts as opposed to acidic catalysts. Investigations designed to provide this information are in progress.

Summary

1. The ammonolysis of 2-chlorobenzothiazole by liquid ammonia has been shown to be a pseudo-unimolecular reaction which is not appreciably catalyzed by relatively high concentrations of

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[15] The experimental methods employed did not permit an exact determination of the concentration of ammonia, but a reasonably accurate value was obtained by measuring the volumes of the 2-chlorobenzothiazole and ammonia in the reaction tube (at 25°) before mixing. From the density of liquid ammonia at 25° [Plank and Hunt, THIS JOURNAL, **61**, 3590 (1939)] the concentration was calculated. The specific reaction rate was then calculated. The resulting values (7.29×10^{-5}, 7.14×10^{-5}, and 6.70×10^{-5}) agree within the limits of the errors involved in the calculations.

[16] Makishima, *J. Faculty Eng., Tokyo Imp. Univ.*, **21**, 115 (1938).

neutral salts or of salts which behave as acids in liquid ammonia.

2. Values for the reaction velocity constant, temperature coefficient, and energy of activation have been calculated.

3. The most probable reaction mechanism is concluded to be that involving a bimolecular reaction between molecules of the thiazole and molecules of ammonia.

AUSTIN, TEXAS RECEIVED MARCH 22, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Ketene and the Structure of Methylene

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According to Pearson, Purcell and Saigh,[1] methylene produced either thermally or photochemically by the decomposition of ketene at low pressures behaves more like a very reactive molecule than like a free radical. Its half-life before reaction, measured by the Paneth streaming method,[2] runs up to 5×10^{-2} sec. or greater in ketene at $\sim$1.5 mm. pressure and up to 2.3×10^{-1} sec. in nitrogen, but is much less in a stream of diazomethane. On the other hand, the work of Ross and Kistiakowsky[3] on the photolysis of ketene clearly shows that free methylene, presumably formed in the reaction, reacts rather readily with ethylene when it is present in large excess and that under such conditions no additional ethylene is formed.

As will be shown below, knowledge of the precise structure of methylene is of value both for its own sake and because of its implications in connection with other problems. Fortunately, a simple device for distinguishing between free radicals and reactive molecules presents itself in the previously studied reaction[4]

$$R + NO \longrightarrow RNO \qquad (1)$$

where R is a free radical. In the investigation herein reported we have studied the photolysis of ketene over a restricted range of temperature in the presence of varying concentrations of nitric oxide and ethylene.

Experimental

Chemicals.—Nitric oxide was prepared, as previously described[5] and tapped off at will. We found that the most convenient source of ketene was from the pyrolysis of diketene somewhat as described by Boese,[6] although we were not able to obtain a product of as high purity as is recorded in the literature. Fortunately, repeated freezing, distillation and evacuation of our ketene rid it of acetone and other high-boiling impurities, leaving behind only such ethylene, nitrogen and traces of hydrocarbon gas as could not be conveniently removed. Since the reactions were followed analytically, the presence of non-interfering impurities was not particularly troublesome. Tank ethylene was withdrawn as required and purified by repeated freezing in liquid nitrogen, evacuation, and melting before use.

Apparatus.—The apparatus was substantially as already described in the study of the photolysis of azomethane.[7] A General Electric H-4 high pressure mercury vapor lamp without the glass envelope was used as a light source. It was situated about 5 cm. from the 1-liter Pyrex bulb (of accurately known volume) which was used as the reaction vessel. The temperature of the latter was controlled by immersion in a beaker filled with water and maintained manually at constant temperature within about 0.2°. Pyrex cuts off light at slightly less than 3000 Å. so that the full strength of the arc at longer wave lengths was available for photolysis. Since the ketene absorbs and is decomposed by light of λ 3130 Å.,[3] this arrangement proved adequate.

Technique.—Samples of ketene to be photolyzed were introduced into the reaction vessel at known temperature and pressure. Changes in pressure were followed on a mercury manometer. Samples were withdrawn from the vessel for macro-gas analysis both prior and subsequent to reaction. From the percentage composition so determined, the volumes at S. T. P. of gases produced and consumed in the reaction could be determined.

In the early work only the ketene was analyzed initially. In later work (*i. e.*, beginning with Experiment 20) the entire reactant gas was analyzed. (It is known now that there is little advantage in that practice.) The procedure for analyzing the reactant gas was simply to pass it through a small "B-D" auto-bubbler pipet[8] containing standard sodium hydroxide of known volume and then into a Fisher Gas-Analyzer. Nitric oxide was determined by volume decrease in potassium hydroxide after mixing with oxygen

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[1] Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938).

[2] *Cf.* F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335 (1929).

[3] W. F. Ross and G. B. Kistiakowsky, THIS JOURNAL, **56**, 1112 (1934).

[4] *Cf.* G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 118.

[5] Davis, Jahn and Burton, THIS JOURNAL, **60**, 10 (1938).

[6] A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 16 (1940). We are indebted to the Carbide and Carbon Chemical Corp. for the gift of the diketene used.

[7] Burton, Davis and Taylor, THIS JOURNAL, **59**, 1038 (1937).

[8] M. Burton and T. W. Davis, *Ind. Eng. Chem., Anal. Ed.*, **9**, 139 (1937).