analyses are possibly not very accurate (*e.g.*, for expt. 10 and 18 ($[\mathrm{TSN}]_\infty + 2[\mathrm{IBN}]_\infty)/[\mathrm{AZO}]_0$ is lower than expected). Mechanism 1–4 can be modified exactly to include IBN and MAN production without changing the form of (5)–(9) and their analogs[5] or the essential meaning of k_4U and V. The concomitant formation of 2,3,5-trimethyl-2,3,5-tricyanohexane, TTH, can be handled assuming MAN is readily attacked by R· radicals and equating $\mathrm{RCH_2}$-CH(CN)· with R· and the ketenimine isomers[3] of TTH with DKI, the resulting errors being probably undetectable in the above results when $[\mathrm{IBN}]_\infty/[\mathrm{TSN}]_\infty$ is 0.06 ± 0.02. Consequently, if true molecular decomposition paths for AZO and DKI are absent and R· radicals react in the same way inside and outside the cited reaction cages, DKI, TSN and IBN molecules form the R· radicals in the approximate proportion $0.5_7:0.4_1:0.0_2$.

The maximum values of k_4Ut, denoted by k_4Ut^*, that satisfy (A7) are listed in Table AII also, together with the corresponding data for $k_4Ut_{\max}$ and $k_1t_{\max}$. Table AII shows, for example, that $t_h < t^* \geqslant t_{\max}$ providing *ca.* $0.70 \leqslant k_1/(k_4U) \leqslant$ *ca.* 1.43, where t_h is the time for half consumption of AZO, *i.e.*, $0.693/k_1$. This indicates a considerable range of reaction times for which (9) is a suitable approximation. It should be mentioned that (A6) and (A7) are comparatively strict conditions that could be relaxed somewhat with corresponding gain in the range of satisfactory applicability of (9).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

A Study of the Kinetics of the Chloramine–Ammonia and Chloramine–Hydrazine Reactions in Liquid Ammonia[1]

BY FRANCIS NASH COLLIER, JR.,[2] HARRY H. SISLER, JACK G. CALVERT AND FORREST R. HURLEY

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The rate of the hydrazine forming reaction between chloramine and ammonia in liquid ammonia solution was followed conductimetrically at five temperatures. The reaction was found to be pseudo-first order, its rate independent of ionic strength and acidity in ammonia solutions of ammonium chloride from 0.001 to 0.01 molar. From the temperature dependence of the rate constants the energy and entropy of activation were obtained. The stoichiometry and rates of the hydrazine decomposition reaction simultaneously occurring between chloramine and hydrazine in the same solution were investigated. The formation reaction has a higher temperature coefficient than the decomposition reaction, allowing higher yields of hydrazine at higher temperatures. An induction period in the decomposition reaction endures long enough to permit useful yields of hydrazine to be formed, even though the decomposition reaction is the faster of the two. The induction period is prolonged by decreasing concentrations of chloramine and hydrazine, accounting for higher yields at lower concentrations. A free radical chain mechanism for the decomposition reaction is considered.

Introduction

Mattair and Sisler[3] describe a process in which hydrazine is synthesized by the action of chloramine on liquid ammonia. The chloramine reacts slowly with ammonia to form hydrazine.

$$\mathrm{NH_2Cl + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl} \qquad (1)$$

Yields in this process are reduced by a hydrazine consuming side reaction for which the following equation is proposed

$$\mathrm{N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl} \qquad (2)$$

Raschig[4] studied the synthesis of hydrazine in aqueous ammonia in the presence of fixed base and reported the over-all equation for the formation and decomposition reactions

$$\mathrm{3NH_2Cl + 3OH^- \longrightarrow N_2 + NH_3 + 3Cl^- + 3H_2O} \qquad (3)$$

Joyner[5] suggested that the decomposition of ammonia by chloramine in the Raschig process probably passed through the intermediate hydrazine, and that the latter was oxidized in accordance with equation 2.

Laitinen[6] suggested the alternate equation

$$\mathrm{2N_2H_4 + NH_2Cl \longrightarrow N_2 + 2NH_3 + NH_4Cl} \qquad (4)$$

as representing the possible stoichiometry of the decomposition reaction in liquid ammonia. However, the stoichiometry was not established experimentally.

Though Bodenstein[7] studied the kinetics of the Raschig synthesis, he followed the sum of the formation and decomposition reactions. Nowhere is information available concerning rates of the separate reactions. However, there is an abundance of yield data[5,8,9] at hand.

Cahn and Powell[10] were able to obtain relative rate constants for formation and decomposition reactions using the yield data of Joyner obtained for the Raschig synthesis. Sisler, Neth and Hurley[9] obtained yield data for the reactions in liquid ammonia and showed that increase in temperature, decrease in concentration of reactants, and decrease in ammonium chloride concentration all had favorable influence on yields of hydrazine. But, in spite of what had been accomplished, it was felt that quantitative kinetic data would be of assistance in clarifying the mechanisms of the reactions.

Experimental Details

Preparation and Purification of Reagents. (a) Solvent Ammonia.—Verkamp anhydrous ammonia was purified by condensing it from the cylinder directly into the conductivity cell or other receiver.

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[1] Abstracted from the Ph.D. dissertations of F. R. Hurley, The Ohio State University, 1954, and of F. N. Collier, Jr., The Ohio State University, 1957, the latter available on microfilm from University Microfilms, Inc., Ann Arbor, Michigan.

[2] Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina.

[3] R. Mattair and H. Sisler, THIS JOURNAL, **73**, 1619 (1951).

[4] F. Raschig, "Schwefel-und-Stickstoff Studien," 1st Ed., Verlag Chemie, G. m. b. H., Berlin, 1924, p. 73.

[5] R. Joyner, *J. Chem. Soc.*, **123**, 1114 (1923).

[6] H. A. Laitinen, "Lower Oxidation States in Liquid Ammonia," Final Report to the Office of Naval Research, Contract NONR 21900 NRO 52247.

[7] M. Bodenstein, *Z. physik. Chem.*, **139a**, 397 (1928).

[8] M. Jones, L. Audrieth and E. Colton, THIS JOURNAL, **77**, 2701 (1955).

[9] H. Sisler, F. Neth and F. Hurley, *ibid.*, **76**, 3909 (1954).

[10] J. Cahn and R. Powell, *ibid.*, **76**, 2565 (1954).

(b) **Ammonium Chloride.**—Mallinckrodt analytical reagent grade ammonium chloride dried over sulfuric acid was used for calibration of the conductivity cell. Ammonium chloride formed in the chloramine generator was used when it was desired to test the effect on rate of adding ammonium chloride to the reaction mixture. It was thought to be free of traces of metal ions since it had not been recrystallized from water.

(c) **Chloramine.**—Chloramine was prepared by the gas phase reaction of chlorine with ammonia in a Sisler-Mattair[3,11] generator. The effluent gases were condensed in a receiver containing liquid ammonia.

(d) **Hydrazine.**—Anhydrous hydrazine manufactured by both the Matheson and the Fairmount Chemical Companies was used. It was freed of water by distilling over flake caustic at reduced pressure.

Apparatus.—The apparatus employed in the conductivity measurements consisted of the conductivity cell, the conductivity bridge, auxiliary capacitances, the thermostatic bath and its control equipment, and accessory glassware, baths, and manometers used in condensing and transferring ammonia and its solutions. Figure 1 provides a view of the assembled apparatus and the accompanying legend describes most of the parts.

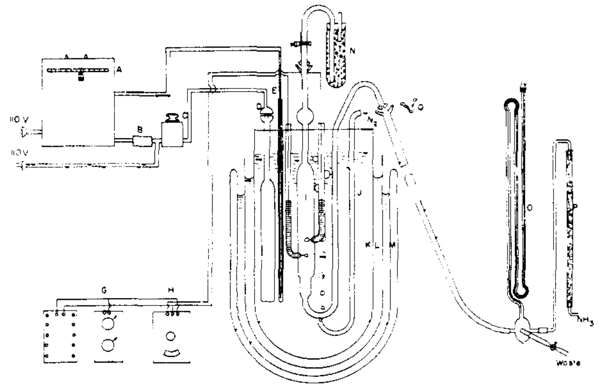

Fig. 1.—Apparatus assembled for making rate measurements: A, Leeds and Northrup Micromax self recording potentiometer with control circuit; B, relay; C, powerstat; D, Cenco knife heater; E, No. 38 copper-constantan thermocouple encased in 3 mm. glass tube; F, decade condenser, 0.001–0.010 µfd; G, decade condenser, 0.01–0.10 µfd.; H, Industrial Instruments model RC16 conductivity bridge; I, conductivity cell; J, mixing gas inlet tube for thermostatic bath; K, container for inner bath; L, container for intermediate bath; M, dewar container for outer bath; N, drying tube; O, manometer used in condensing ammonia; P, glass wool filter for ammonia gas; Q, cover for capillary of conductivity cell.

(a) **Conductivity Cell.**—The conductivity cell is also shown in Fig. 1. Bright platinum wire loop electrodes were used to minimize possible catalytic decomposition of hydrazine at their surfaces. The electrodes were sealed into the Pyrex envelope of the cell through a graded seal. Platinum tipped lead wires made contact with the electrodes through mercury pools in the side arms of the cell.

(b) **Conductivity Bridge.**—Industrial Instruments conductivity bridge, Model R. C. 16, was used and all measurements were made at 1000 c.p.s. Auxiliary capacitances in decades from 0.001 to 0.10 µfd. were used to balance out capacity effects in the circuit.

(c) **Thermostatic Bath.**—A bath easily adjusted over widely spaced temperature intervals was employed. It was externally cooled by a Dry Ice bath and internally but intermittently heated by a Cenco immersion knife heater. A Leeds and Northrup Micromax self recording potentiometer with control circuit was used to control the heating. When the bath was operated at temperatures much higher than that of Dry Ice, a jacket was introduced between the bath proper and the cooling mixture. Both the bath and its jacket were filled with acetone. The bath proper was stirred by a rapid stream of dry nitrogen. Temperature within the bath was controlled from ± 0.5° at −75° to ±1.0 at −38°. To minimize temperature errors, conductivity readings were made at the same point in the heating cycle where possible.

Procedure. (a) **Calibration of the Conductivity Cell.**—The conductivity cell was calibrated over concentration ranges encountered in the experiments by introducing weighed quantities of ammonium chloride into known volumes of liquid ammonia contained in the conductivity cell. A separate calibration was made for each temperature at which the cell was to be used.

(b) **Measurement of Reaction Rates.**—Since both formation and decomposition reactions (equations 1 and 2) were to be studied, experimental conditions were selected such as to emphasize one reaction and repress the other, as the experiment demanded. If the reaction mixture was initially very low in hydrazine, or lacked hydrazine altogether, the formation reaction occurred alone. See Fig. 3, experiments 3, 28 and 29. If the mixture initially contained low to moderate quantities of hydrazine, the decomposition reaction also occurred after a period of induction had elapsed. See Fig. 2, experiments 9 and 12.

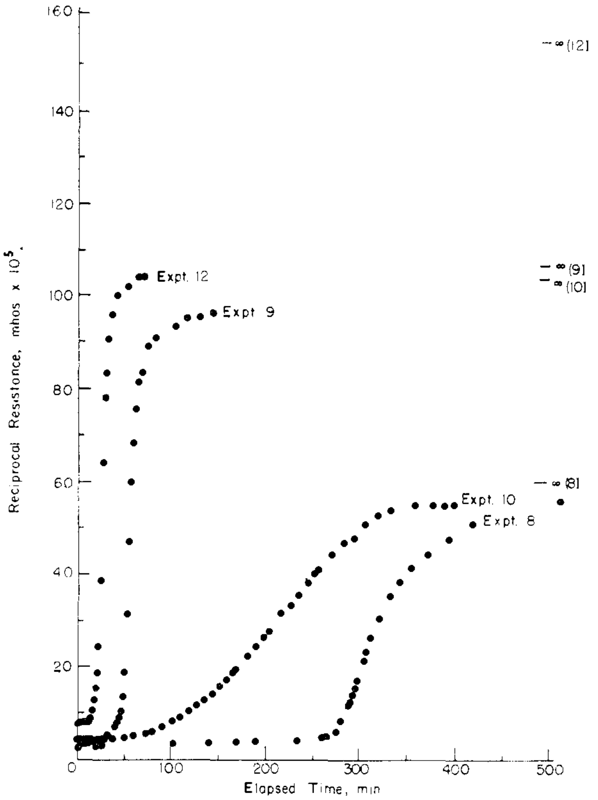

Fig. 2.—Rate measurement data for mixtures initially containing hydrazine.

The reaction mixture used in a study of the formation reaction contained initially only chloramine at a concentration of 0.015–0.030 M in the solvent, ammonia, which was also a reactant. Small quantities of hydrazine and ammonium chloride were formed before the mixture could be introduced into the conductivity cell. These quantities were minimized by condensing the chloramine from the generator directly into the solvent ammonia at −77°. This served to dilute and cool the reactants. The solution of chloramine was transferred to the conductivity cell and diluted to the volumetric line with ammonia. It was mixed for several minutes by a slow stream of dry nitrogen while it came to bath temperature. Resistance values were recorded against elapsed time. Brief mixing was repeated six or eight times in the first 20 min. and occasionally thereafter. The course of the reaction usually was followed for 600–900 min.

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(11) H. Sisler, F. Neth, R. Drago and D. Yaney, THIS JOURNAL, **76**, 3906 (1954).

The reaction was terminated by the addition of a large excess of hydrazine. All the unreacted chloramine was converted at once to ammonium chloride. After the solution was mixed the resistance was noted. The volume of the solution was noted before and after the terminal addition of hydrazine.

The reaction mixture used in a study of the decomposition reaction, equation 2, contained, initially, chloramine and half equivalent quantities of hydrazine with small quantities of ammonium chloride and hydrazine originating as explained. The hydrazine was weighed from a hypodermic syringe and introduced into 10–15 ml. of liquid ammonia in a separate receiver. The solution was mixed with dry nitrogen and transferred to the conductivity cell which already contained the chloramine solution. The cell contents were diluted to the volumetric line with liquid ammonia. The solution was mixed and the progress of the reaction was followed as already described.

(c) **Measurement of the Stoichiometry of the Decomposition Reaction.**—The stoichiometry of the decomposition reaction was established by three independent methods. Two of the three utilized data obtained in the course of the rate studies, but the third method, that of gas evolution, required a special procedure. The volume of nitrogen evolved was compared with the ammonium chloride formed during the decomposition reaction.

In order to bring the reagents together at high concentrations of hydrazine in such a way that the reaction could be controlled while the gas was being collected, excess hydrazine, dissolved in ammonia, was frozen at the bottom of the conductivity cell. It was overlayered with the chloramine solution. The cell contents were allowed to melt, mix by diffusion and react. The gas evolved was measured in a mercury filled gas buret. The ammonium chloride formed was determined from the conductivity of the solution and its volume.

Data and Results

Calculations. (a) **Calibration Data.**—Examination of the calibration data of the conductivity cell revealed that a plot of the logarithm of the reciprocal cell resistance against the logarithm of the ammonium chloride concentration gave a straight line over the concentration regions covered in the calibrations. This observation is, in general, in accord with equation 5

$$\log (\lambda^0 - \lambda) = n \log c + \text{constant} \qquad (5)$$

described by Harned and Owen.[12] When solved for the concentration of ammonium chloride, the usual slope intercept equation becomes

$$\log [\mathrm{NH_4Cl}] = 1/a \log (\text{recip. resist.}) - b/a \qquad (6)$$

In the antilog form this is

$$[\mathrm{NH_4Cl}] = 10^{-b/a} (\text{recip. resist.})^{1/a} = B\,(\text{recip. resist.})^A \qquad (7)$$

where it is convenient to define the terms $1/a$ and $10^{-b/a}$ as A and B, respectively.

(b) **Calculation of Corrected Final Concentration.**—The chloramine remaining unreacted in the solution at the end of the rate measurements was converted rapidly to ammonium chloride through reaction with excess of hydrazine added terminally (see Experimental Details). From the resistance of the solution and the volume changes accompanying the addition of hydrazine a final ammonium chloride concentration, C_F, corrected for dilution by hydrazine was obtained.

The value of C_F includes all the ammonium chloride present, regardless of the source. It should be noted that one mole of chloramine forms one mole of ammonium chloride when consumed in either the formation or decomposition reactions, equations 1 or 2. Hence the chloramine initially present in the reaction mixture can be obtained from the difference in the value of C_F and the initial ammonium chloride concentration. The concentration of chloramine remaining unreacted at any time during a rate experiment was calculated by the difference in C_F and the ammonium chloride concentration in the solution at that time as shown in equation (8)

$$[\mathrm{NH_4Cl}] = C_F - B(\text{recip. resist.})^A \qquad (8)$$

(c) **Calculation of Hydrazine Concentration.**—The concentration of hydrazine in the reaction mixture at a given time can be computed by the following method provided that the initial reaction mixture contains a stoichiometric excess of chloramine. The data essential to the calculations are values of the concentration of ammonium chloride in the reaction mixture (1) initially, (2) at the given time and (3) at the point of the "break" (described below). Several rather well justified assumptions about the course of the reaction must be made to apply these calculations properly (see Discussion).

It must be assumed that the formation reaction, equation 1, proceeds alone and practically uncomplicated by the decomposition reaction for a variable but definitely observable portion of the course of the reaction, while the decomposition reaction, equation 2, is passing through a period of induction. Within this region the stoichiometric relations of the formation reaction are obeyed and the increase in hydrazine concentration, therefore, equals the increase in ammonium chloride concentration

$$\Delta[\mathrm{N_2H_4}] = B(\text{recip. resist.})^A - B(\text{recip. resist.})_0^A \qquad (9)$$

The concentration of hydrazine must be adjusted for any hydrazine added initially.

It must be assumed that the decomposition reaction, equation 2, begins suddenly, and since it is very much faster than the formation reaction at low temperatures, it proceeds substantially alone until the hydrazine in the solution is consumed. (For the effect of temperature, see Discussion, Decomposition reaction part c.)

When a reaction mixture containing chloramine and hydrazine is first prepared it reacts slowly. Then a sudden increase in rate is noted. The beginning point of the rapid reaction will be called the "break." It corresponds with the onset of the decomposition reaction. The decomposition reaction ends when the hydrazine present has been consumed. It is followed by a second region of slow reaction. The point of transition from the rapid decomposition reaction to the second region of slow reaction may be noted on the graphs and corresponds with the end-point of the decomposition reaction.

In the region from the break to the end-point of the decomposition reaction, hydrazine is decomposing rapidly. The quantity of hydrazine gained from the formation reaction in this region may be regarded as insignificant at the lower temperatures. Hence the increase in ammonium chloride concentration in this region is considered to measure hydrazine loss alone. In accord with

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[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed. Rev., Reinhold Publ. Corp., New York, N. Y., 1950, pp. 155–156.

equations 2 and 7, this may be expressed for a given time t within the region as

$$\Delta[\mathrm{N_2H_4}] = -B/2\ [(\text{recip. resist.})_{\mathrm{t}}^{A} - (\text{recip. resist.})_{\mathrm{break}}^{A}] \qquad (10)$$

Thus if the reaction is allowed to proceed from the break to the end-point, the total number of moles of hydrazine consumed, originating from all sources, must have equaled half the number of moles of ammonium chloride formed. This is true provided the stoichiometric relation expressed in equation 2 applies and if chloramine is initially present in excess.

(d) **Derivation of an Expression for the Rate Constant of the Formation Reaction.**—The rate of the formation reaction, shown in this work to be first order with respect to chloramine concentration, can be expressed in terms of the reciprocal resistance of the solution and the calibration data of the conductivity cell. The relation

$$-\frac{\mathrm{d}[\mathrm{NH_2Cl}]}{\mathrm{d}t} = \frac{+\mathrm{d}[\mathrm{NH_4Cl}]}{\mathrm{d}t} = k_1[\mathrm{NH_2Cl}]^n \qquad (11)$$

can be expanded by replacing the concentration of chloramine by its equivalent from equation 8. The first derivative of the ammonium chloride concentration with respect to time can be replaced by the product

$$\frac{\mathrm{d}[\mathrm{NH_4Cl}]}{\mathrm{d}(\text{recip. resist.})} \times \frac{\mathrm{d}(\text{recip. resist.})}{\mathrm{d}t} \qquad (12)$$

The first term of this product can be expressed by taking the derivative of the ammonium chloride concentration with respect to reciprocal resistance in equation 7 and the second term as simply the slope of the rate measurement graph (plotted as reciprocal resistance *vs.* time). On solving for k_1, this becomes

$$k_1 = \frac{AB(\text{recip. resist.})^{A-1}\,\dfrac{\mathrm{d}(\text{recip. resist.})}{\mathrm{d}t}}{[C_{\mathrm{F}} - B(\text{recip. resist.})^{A}]^{n}} \qquad (13)$$

Stoichiometry of the Decomposition Reaction.—The stoichiometry of the decomposition reaction was verified in three different types of measurement: (a), (b) and (c).

(a) **Measurement by the Method of Gas Evolution.**—The number of moles of ammonium chloride formed to moles of nitrogen evolved in the decomposition reaction were compared. A correction was applied to the moles of ammonium chloride formed in the decomposition reaction for that formed by the formation reaction which was proceeding concurrently.

(b) **Measurement by Use of Weighed Samples of Hydrazine.**—The measurement of the ratio of the number of moles of ammonium chloride formed to moles of hydrazine consumed in the decomposition reaction is obtained in the course of studying the rate of the decomposition reaction. The quantity of hydrazine used was measured by weighing it into solutions containing excess of chloramine. The ammonium chloride formed during the decomposition of the hydrazine was measured conductimetrically. Complete reaction was indicated by a sharp decrease in reaction rate at the end-point.

(c) **Measurement by Comparison of Pre-break and Post-break Quantities of Ammonium Chloride.**—In this method, the hydrazine consumed in the decomposition reaction was produced in the reaction mixture by the formation reaction. It was found that in some cases the formation reaction proceeded alone creating hydrazine, and that, after a period of induction, the decomposition reaction set in at a point marked by a break in the rate curve and rapidly consumed this hydrazine. The ammonium chloride formed before the break is the equivalent of the hydrazine formed before the break. The ammonium chloride formed after the break to the end of the rapid decomposition reaction is the equivalent of the chloramine consumed after the break in decomposing this hydrazine. Hence a comparison of the post-break and pre-break accumulation of ammonium chloride was taken as a measure of the stoichiometry of the decomposition reaction.

TABLE I

STOICHIOMETRY OF THE DECOMPOSITION REACTION

Method	Ratio investigated	Av. exptl. value of ratio	No. of independent measurements
Gas evolution	$\frac{\mathrm{NH_2Cl}}{\mathrm{N_2}}$	1.92	10
Weighed samples of hydrazine	$\frac{\mathrm{NH_2Cl}}{\mathrm{N_2H_4}}$	1.69	12
Post-break, pre-break ammonium chloride	$\frac{\mathrm{NH_2Cl}}{\mathrm{N_2H_4}}$	1.95	10

The results by the three methods are compared in Table I. The values 1.92 and 1.95 obtained by the first and third methods, respectively, definitely exclude the stoichiometric relation expressed in equation 4 as a possibility, since equation 4 predicts ratios of 1.00 and 0.50, respectively, for these quantities. The result by the second method is low, possibly because of evaporation of liquid hydrazine as it was dropped into the reaction mixture from the tip of a hypodermic needle.

Rate Measurement Data.—The experiments performed can be classified by types depending on their purposes and the compositions of their reaction mixtures. A condensation of the data is given in Table II. The expression for the specific reaction rate constant is given by equation 13.

Experiments 5 through 22 were carried out using a reaction mixture composed initially of chloramine and hydrazine in liquid ammonia. These experiments were devised for the purpose of studying the decomposition reaction at −75°. Plots of the data showed that the decomposition reaction exhibited an extremely variable induction period, ranging from a few minutes to several hundred minutes. Typical plots of rate data are shown in Fig. 2. In general the induction period was found to be shorter at higher hydrazine and chloramine concentrations. (See Discussion, The Decomposition Reaction part e.) Experiments 14 through 18 and 41 through 44 will be described in the same section of the Discussion.

During the induction period of the decomposition reaction, it was found possible in many cases to measure the rate constants of the formation reaction. However, most of the experiments 5

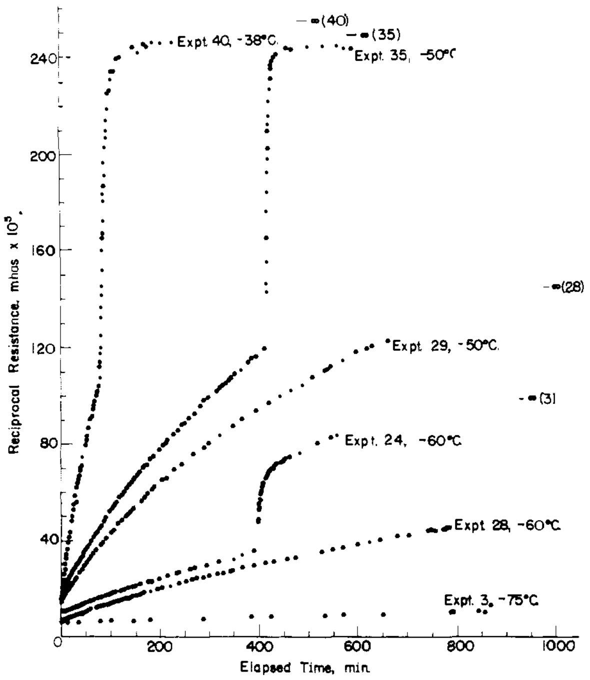

Fig. 3.—Rate measurement data for mixtures initially containing no hydrazine.

through 22 had relatively short pre-break regions and the formation reaction was in the process of merging with the decomposition reaction from the beginning. When the induction period was long enough to provide a small section of the rate measurement graph in the pre-break region, it was found that the formation rate constants were equal within the larger experimental error to the values obtained from purely formation reaction experiments at that temperature.

Though rate constants of the decomposition reaction were not obtained, the course of the decomposition reaction could be followed, practically unobscured by the formation reaction, at the lower temperatures investigated. The decomposition reaction can be seen to be very much more rapid than the formation reaction and itself very little temperature dependent (see Figs. 2 and 3).

Experiments 1 through 4 and 23 through 40 were carried out using reaction mixtures consisting of chloramine in liquid ammonia. The experiments were for the purpose of studying the kinetics of the formation reaction at the temperatures −75, −60, −50 and −38°. See Fig. 3 and Table II.

However, in a progressively larger fraction of the experiments as the temperature was elevated, the decomposition reaction also occurred. The decomposition reaction set in very abruptly after the formation reaction had created sufficient hydrazine (while sufficient chloramine was yet present) to favor it. (See Discussion, Decomposition Reaction, part e.)

At higher temperatures, the induction period was shorter than at lower temperatures, partly, at least, because less time was needed to create the hydrazine which would be consumed in the following decomposition reaction.

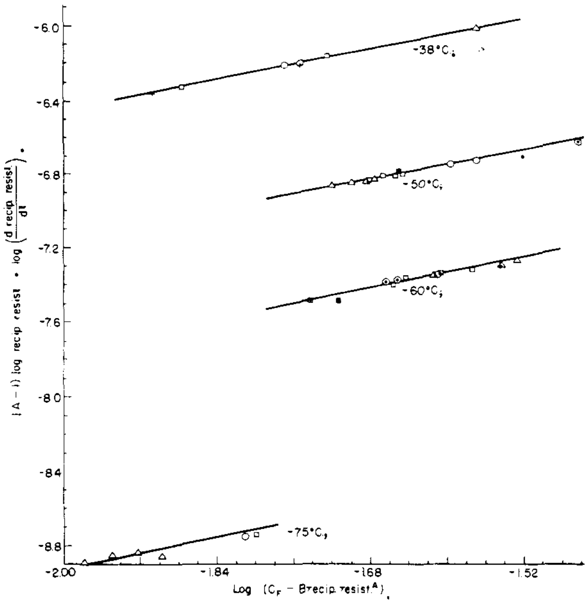

Fig. 4.—Order of the formation reaction with respect to chloramine concentration.

The decomposition reaction was not observed at all at −75° with reaction mixtures initially containing no hydrazine even after 7200 min. in the case of experiment 4 (though it probably would have occurred if the chloramine had been at considerably higher concentrations). It was observed only once at −60° and that after 400 min., four times in 150 to 425 min. at −50°, but in every experiment in as little as 70–150 min. at −38°.

The formation reaction was allowed to proceed until it was superseded by the decomposition reaction. If the decomposition reaction did not occur within 500 to 1000 min. the formation reaction was terminated by the addition of excess hydrazine.

It should be noted that the values of the rate constants were found to be invariant over the entire observed course of the reaction. Values computed by equation 13 are shown in Table II.

Experiments 41 through 44 at −38° gave formation rate constants in their pre-break regions which were of the order of magnitude expected for the reaction at that temperature, 330–570 $\times 10^{-5}$ min.$^{-1}$ in the fourteen test calculations made on them, though the special cell in which the measurements were made was too crudely designed to yield accurate rate measurement data.

Order of the Formation Reaction.—In the expression for the rate constant, equation 13, the order of the formation reaction with respect to chloramine is assigned the value n. The reaction is treated as if it were zero order with respect to the solvent, ammonia. In log form equation 13 leads to an equation in the plot of which the slope is n and the intercept is $\log k_1/AB$.

The results of applying this equation to the data are shown in Fig. 4. Points on the graphs were obtained from three, six, six and four independent rate measurement experiments at −75, −60, −50 and −38°, respectively. Several values were selected from each experiment at several

TABLE II

REACTION RATE MEASUREMENT DATA

	Initial compn. of reaction mixture		Similar to exp. shown in Figs. 2 or 3	Length of induction period	Reactions observed	Rate constants	
Expt. no.	Chloramine, mole/l.	Hydrazine, mole/l.	Exp. no.	of decn. reaction, min.	Exp. no.	$k \times 10^5$, min.$^{-1}$	Elapsed time, min.
			Experiments at −75°				
1	0.012	None	3	No break	1	2.22	375
2	.015	None	3	No break	1	3.21	313
3	.016	None	3	No break	1	3.19	532
4	.013	None	3	No break	1	3.10	210
						3.48	1950
						3.45	3700
						3.42	5650
5	.019	0.0125	12	20	2		
6	.018	.0052	9	80	2		
8	.008	.0053	8	270	1,2		
9	.017	.0090	9	45	2		
10	.017	.0047	10	85	2		
12	.029	.0095	12	15	2		
13	.021	.0048	10	190	1,2		
14	.023	.0050	12	8	2		
15	.019	.0053	12	10	2		
16	.028	.0046	12	15	2		
17	.019	.0046	9	7	2		
18	.025	.0046	9	18	2		
19	.017	.0046	12	5	2		
20	.007	.0047	9	58	2		
22	.022	.0044	9	20	2		
			Experiments at −60°				
23	0.025	None	28	No break	1	30.4	50
						29.0	130
						30.9	228
						30.4	375
						27.9	475
24	.022	None	24	400	1,2	30.1	25
						29.6	88
						29.7	188
						30.6	325
25	.027	None	28	No break	1	28.0	80
						29.9	275
						29.0	335
						30.8	525
						30.5	575
26	.028	None	28	No break	1	27.3	48
						26.7	135
						26.0	265
						27.0	410
						29.8	628
						29.2	728
						28.0	828
27	.029	None	28	No break	1	30.0	50
						28.5	106
						28.0	380
						28.7	612
						27.4	800
28	.019	None	28	No break	1	26.6	38
						27.5	93
						28.7	263
						28.4	538
						26.7	675
			Experiments at −50°				
29	0.026	None	29	No break	1	104	20
						109	95
						108	155
						102	263
						97	388
						115	563
						112	600
30	.027	None	35	130	1,2	105	13
						111	33
						106	70
						109	100
31	.023	None	35	325	1,2	98	15
						104	53
						103	99
						103	153
						101	200
						122	256
						110	295
32	.022	None	35	310	1,2	106	8
						106	23
						105	48
						106	80
						101	135
						108	213
						112	270
33	.021	None	29	No break	1	104	10
						105	28
						106	65
						106	105
						102	180
						111	278
						103	383
						106	525
						109	705
34	.028	None	35	105	1,2	101	5
						104	38
						102	75
35	.034	None	35	420	1,2	105	13
						105	60
						108	83
						107	143
						110	255
						109	338
			Experiments at −38°				
36	0.019	None	40	40	1,2	456	7
						441	25
						425	34
37	.023	None	40	65	1,2	482	3
						499	5
						421	18
						417	37
						427	55
38	.018	None	40	105	1,2	448	9
						454	18
						428	26
						432	55
						426	73
						439	93
39	.019	None	40	135	1,2	455	5
						449	18
						480	31
						474	53
						454	82
						461	97
40	.029	None	40	75	1,2	468	6
						449	20
						430	31
						429	56
41	.019	None	40	75	1,2		
42	.028	None	40	65	1,2		
43	.041	None	40	110	1,2		
44	.035	None	40	145	1,2		

stages during the reaction to test whether the order held over the entire period of observation.

Since the intercept is a function of the temperature, separate straight lines are predicted for each temperature. The separate lines were observed and are narrowly defined by the experimental points. They have the following slopes as measured from a large working graph: 0.95, 0.97, 0.96 and 1.01 at −75, −60, −50 and −38°. The average uncertainty in these slopes is ±0.06. Hence it is established that the order of the reaction with respect to the chloramine concentration is 1.0 within the experimental error, and, from the straight line relation, that the order does not change during the course of the reaction.

Rate Function of the Formation Reaction.—An Arrhenius plot of the data is shown in Fig. 5. Prior work of Hurley[1] at −33° is included for comparison (triangular point). The points plotted are composites of numerous rate constant measurements: seven, thirty-one, forty, twenty-three and fourteen at −75, −60, −50, −38° (more precisely for these calculations −74.3, −60.4, −50.6, −37.9°)

and −33° (Hurley). The least squares treatment of the data leads to an expression for the rate of formation of hydrazine in liquid ammonia in mole/l. sec.

$$\frac{-\mathrm{d}[\mathrm{NH_2Cl}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{N_2H_4}]}{\mathrm{d}t} = [\mathrm{NH_2Cl}]\ 2.90 \times 10^9 e^{-12.7/RT} \qquad (14)$$

At −50.6° the enthalpy of activation, $\Delta H^{\ddagger}$, equals 12.2 kcal./mole and the entropy of activation, $\Delta S^{\ddagger}$, equals −24.0 e.u. (standard states: one mole/l.). These terms of the absolute reaction rate theory were calculated from the second-order rate constant obtained by dividing the apparent first-order rate constant by the constant concentration of ammonia, 41.2 moles/l., at −50.6°.

These values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are consistent with the corresponding values calculated from rate measurements for similar displacement reactions of halogen ions by amines.[13]

Discussion

Mechanism of the Formation Reaction.—Several mechanisms have been proposed to explain the phenomena observed when chloramine reacts with ammonia, both in the Raschig synthesis and in anhydrous ammonia. As is usually true in such cases, there is much that is common to all of them. When yields of hydrazine alone are considered, it should be noted that factors actually unfavorable to the decomposition reaction may instead be regarded as favorable to the formation reaction on which they have no influence at all.

A mechanism for the Raschig synthesis was proposed by Audrieth, Colton and Jones.[14] Chloramine is formed according to the equation

$$\mathrm{NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-} \qquad (15)$$

In the presence of strong base the inductive effect of chlorine labilizes an N–H bond to form the chlorimide ion

$$\mathrm{NH_2Cl + OH^- \longrightarrow NHCl^- + H_2O} \qquad (16)$$

Slow reaction occurs with base, either directly, or after losing chloride ion, to form the imide molecule

$$\mathrm{NHCl^- + B \xrightarrow{\text{slow}} HNB + Cl^-} \qquad (17)$$

or

$$\mathrm{NHCl^- \longrightarrow NH + Cl^-} \qquad (18)$$

$$\mathrm{NH + B \xrightarrow{\text{slow}} NHB \xrightarrow{\text{rearrangement}}} \text{ a hydrazine} \qquad (19)$$

The base may be $\mathrm{NH_3}$, $\mathrm{RHN_2}$, $\mathrm{R_2NH}$ or water.

The mechanism of the Raschig synthesis proposed by Bodenstein[7] and by Cahn and Powell[10] is

$$\mathrm{NH_3 + OCl^- \xrightarrow{\text{fast}} NH_2Cl + OH^-} \qquad (20)$$

$$\mathrm{NH_2Cl + NH_3 \xrightarrow{\text{slow}} (N_2H_5Cl) \xrightarrow{OH^-} N_2H_4 + Cl^- + H_2O} \qquad (21)$$

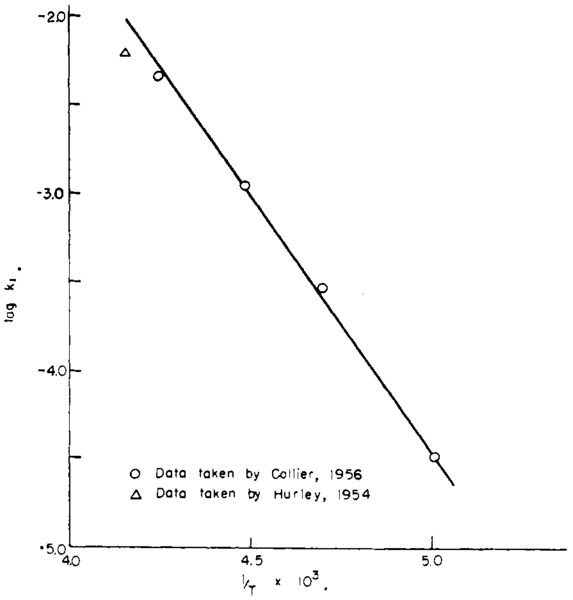

Fig. 5.—Arrhenius plot for the formation reaction.

Wiberg and Schmidt[15] believe that water is essential for the formation of hydrazine from hypochlorite and ammonia or from chloramine and ammonia and that it is essential in either system for the subsequent oxidation of hydrazine to nitrogen, the oxidant in every case being free hypochlorous acid. The steps of the mechanism are

$$\mathrm{ClO^- + H_2O \longrightarrow HOCl + OH^-} \qquad (22)$$

or

$$\mathrm{NH_2Cl + H_2O \longrightarrow NH_3 + HOCl} \qquad (23)$$

$$\mathrm{2NH_3 + HOCl \longrightarrow N_2H_4 + H_2O + HCl} \qquad (24)$$

The decomposition reaction is

$$\mathrm{N_2H_4 + 2HOCl \longrightarrow N_2 + 2H_2O + 2HCl} \qquad (25)$$

The fact that the formation and decomposition of hydrazine occur at all in liquid ammonia either entirely discredits this mechanism if it is presumed that the solvent ammonia is dry, or if the solvent is presumed to be wet, then tests of the mechanism described below under the "Effect of Ammonium Chloride" raise serious objections to it.

These several mechanisms will be evaluated in light of our findings in the sections following.

(a) The Effect of Fixed Base on the Formation Reaction.—Attention is directed to the work of Sisler, *et al.*,[16] who showed that hydrazine could be made in the absence of fixed base not only in anhydrous ammonia but in water and other solvents, though as was pointed out by Jones, Audrieth and Colton,[8] yields were lower. However, Drago and Sisler[17] showed that the best yields in the Raschig process could be obtained when the fixed base was kept always just in excess of the ammonium chloride being formed in the reaction. They interpreted the high yields as due to the fact that excess base destroys chloramine according to the equation

$$\mathrm{3NH_2Cl + 3OH^- \longrightarrow N_2 + NH_3 + 3H_2O + 3Cl^-} \qquad (26)$$

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[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Table V, p. 128.

[14] L. Audrieth, E. Colton and M. Jones, THIS JOURNAL, **76**, 1428 (1954).

[15] E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 336 (1951).

[16] H. Sisler, C. Boatman, F. Neth, R. Smith, R. Shellman and D. Kelmers, THIS JOURNAL, **76**, 3912 (1954).

[17] R. Drago and H. Sisler, *ibid.*, **77**, 3191 (1955).

The Audrieth group formerly thought that the presence of fixed base was essential to the Raschig synthesis[8,14] and considered this as evidence that the acid ionization of chloramine ($pk \approx 14 \pm 2$)[18] was an essential step in the mechanism of the synthesis.

According to the mechanism of Wiberg and Schmidt, equations 24 and 25, the presence of fixed base would reduce the concentration of hypochlorous acid presumed to be present and should reduce the rate of both formation and decomposition reactions. Such an inhibitory effect on the entire process has not been observed.

The fact that fixed base is not essential to the formation of hydrazine favors the mechanism of Bodenstein and of Cahn and Powell.

(b) **Effect of Ammonium Chloride on the Formation Reaction.**—It was known that the presence of ammonium chloride in the reaction mixture reduced the yields of hydrazine in the Raschig synthesis[8] and in the reaction in anhydrous ammonia.[9] It was thought by the adherents of the chlorimide mechanism that the ammonium chloride functioned to decrease the rate of the formation reaction and hence the yield of hydrazine by suppressing the acid ionization of chloramine.

The mechanism of Bodenstein and Cahn and Powell predicts no effect of ammonium chloride on the rate of the formation reaction. The present work provides definite evidence in favor of this mechanism.

The specific reaction rate constants of the formation reaction were measured for more than a score of independent reaction mixtures. The work was done at four temperatures over a tenfold range of ammonium chloride concentration, from 0.001 to 0.010 molar. Periods of observation ranged from a maximum of 7,200 min. at −75° to 150 min. at −38°. These constants were found to be independent of the ammonium chloride concentration. They were constant within less than 5% of the average value of the constant over the whole course of the reaction, or over the portion preceding the onset of the decomposition reaction, with an altogether random scattering of points within the limits mentioned, at the several temperatures.

The results are summarized in the last two columns of Table II and are reported in detail by Collier.[19]

Hurley[1] found for more than a dozen independent reaction mixtures at −33° that the formation rate constants were unaffected by the presence of ammonium chloride in amounts varying from 0.001 to 0.009 molar, a ninefold variation in acidity. The standard deviation of the rate constants for these observations was about 3%. The period of observation was about two hours.

According to the mechanism of Wiberg and Schmidt, if the solvent is presumed to be wet, ammonium chloride should have an accelerating effect on the rate of the formation reaction. According to the chlorimide mechanism (equation 16), it should have a decelerating effect. According to the Bodenstein and Cahn and Powell mechanism it should have no effect. None was observed.

The effect of ammonium chloride on yields in the Raschig synthesis and in the synthesis in liquid ammonia cannot alone be used to test a mechanism since both formation and decomposition reactions may be subject to its influence. Particularly the mechanism of Wiberg and Schmidt is insensitive to such a test as the mechanism predicts both reactions will be accelerated. The effect on yield would depend on the difference in the effect on the two processes.

In order to explain the unfavorable effect of ammonium chloride on yields and at the same time its lack of effect on the formation reaction rate, one is led to accept an hypothesis such as that of Drago and Sisler,[17] *i.e.*, that acid catalyzes the decomposition reaction of hydrazine by chloramine. equation 2. These studies exclude any possibility of the acid catalyzed decomposition of chloramine, at least in the pre-break region, as that would have been reported as acid catalysis of the formation reaction, *i.e.*, acid influence on rate constants.

(c) **The Kinetic Salt Effect.**—It is unlikely that the kinetic salt effect accounts for the decrease in yield produced by ammonium chloride in the synthesis of hydrazine.

This conclusion is based on the studies reported here on the formation reaction and on work of Jones, Audrieth and Colton.[8]

We have shown that the one-one electrolyte, ammonium chloride, does not affect the rate of the formation reaction. The yield studies of Jones, Audrieth and Colton show that the one-one electrolyte, sodium chloride, has no effect on the yield, whereas ammonium chloride decreases it. It is thus demonstrated that electrolyte, as such, neither affects the formation nor decomposition reactions and that the effect of ammonium chloride on yield must be due to its acid character rather than to its nature as an electrolyte. None of the mechanisms considered predicts a kinetic salt effect on the formation reaction.

(d) **The Order of the Formation Reaction.**—It was shown in this investigation that the formation reaction is first order with respect to the chloramine concentration (Fig. 4). The molecularity with respect to ammonia, the solvent, is of course not observable. Since the mechanisms of Bodenstein and Cahn and Powell, equation 21, and of the Audrieth group, equation 17 and 19, both predict unimolecularity with respect to chloramine, the order cannot be used to discriminate between them.

(e) **Quaternary Hydrazinium Salts, Isolated Intermediates of the Formation Reaction.**—Omietanski and Sisler[20] report that chloramine reacts with anhydrous tertiary amines to form the 1,1,1-trisubstituted hydrazinium chlorides which, like other quaternary salts, are not decomposed by base. This discovery was predicted directly by the Bodenstein and Cahn and Powell mechanism

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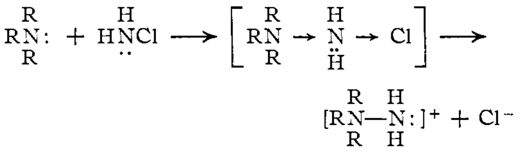
(18) W. Jolly, *J. Phys. Chem.*, **60**, 507 (1956).

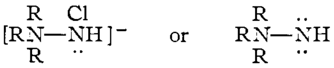
(19) F. N. Collier, Jr., Ph.D. dissertation, The Ohio State University, 1957, Table 50.

(20) G. Omietanski and H. Sisler, THIS JOURNAL, **78**, 1211 (1956).



$$R\overset{R}{\underset{R}{N}}\!: + H\overset{H}{\underset{\cdot\cdot}{N}}Cl \longrightarrow \left[R\overset{R}{\underset{R}{N}} \rightarrow \overset{H}{\underset{\ddot{H}}{N}} \rightarrow Cl\right] \longrightarrow [R\overset{R}{\underset{R}{N}}-\overset{H}{\underset{H}{N}}\!:]^{+} + Cl^{-} \quad (27)$$

The chlorimide mechanism leads to the same final product but arrives at it through one of the intermediates shown



$$[R\overset{R}{\underset{R}{N}}-\overset{Cl}{\underset{\cdot\cdot}{N}}H]^{-} \quad \text{or} \quad R\overset{R}{\underset{R}{N}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}H$$

The intermediates must enter exchange reactions with the solvent to become hydrazinium ions.

The Decomposition Reaction.—Because of the complicated behavior of the decomposition reaction, a detailed knowledge of its kinetics was not achieved as was done in the case of the formation reaction. However, much new information was obtained which should be of help in interpreting yield data and in selecting the best conditions for synthesis of hydrazine. The eccentricities of the decomposition reaction were revealed in a manner that the study of yield data[10] alone would not be likely to suggest.

(a) **Stoichiometry of the Decomposition Reaction.**—As has been reported in Table I the stoichiometry of the decomposition reaction in liquid ammonia was verified in three ways and was found to conform with that expressed in equation 2.

(b) **Separation of Formation and Decomposition Reactions.**—Experimental conditions were controlled to emphasize one or the other of the reactions. When it was desired to study the formation reaction, chloramine in low concentrations, but no hydrazine, was added to liquid ammonia. The decomposition reaction did not occur or else passed through a period of induction under these conditions before it became effective. It was during this period that the formation reaction was observed to occur virtually alone.

When it was desired to study the decomposition reaction, chloramine and hydrazine, both in low concentrations, were added to liquid ammonia. The formation reaction was retarded until it was almost negligible by reducing the temperature to −75° (see section c immediately following). Due to the presence of added hydrazine, the induction period in the decomposition reaction was considerably diminished as in experiments 5 through 22 (Fig. 2), so that the formation portion of the reaction often was obscured

It might be expected that as soon as the formation reaction produced any hydrazine the decomposition reaction would begin to occur. That it did not occur to a detectable extent during an extended period of induction in the decomposition reaction is evidenced by the constancy of the formation rate constants over the interval (see Table II).

If the decomposition reaction were occurring before the break, it would be expected to consume some of the hydrazine formed before the break and the post-break rise in ammonium chloride would not be twice the pre-break rise.

Further evidence that the sudden departure from the established course of the reaction at the break is not merely the acceleration of the formation reaction through some means but is due to the initiation of the decomposition reaction is derived from the fact that the hydrazine formed before the break is consumed after the break.

It is hardly a coincidence that nitrogen as predicted by equation 2 is evolved from the mixture in quantity, both from the body of the solution and from the walls of the cell as well—beginning a minute or two immediately following the break and continuing for some time thereafter. It is never evolved before the break, though the pre-break period may last from 75 to 400 min. depending on temperature and concentration. In mixtures not exhibiting a break, nitrogen is not evolved. Since the solution is mixed periodically with a stream of dry nitrogen, the evolution at the break point in the reaction cannot be ascribed to delay in attaining saturation of the solution with nitrogen.

(c) **Temperature Coefficients of the Formation and Decomposition Reactions.**—The Arrhenius activation energy, E_a, for the formation reaction was found to be 12.7 kcal./mole.

Though rate constants were not obtained for the decomposition reaction., inspection of graphs of all the rate measurements made makes it clear that the decomposition reaction, though many times faster than the formation reaction at all the temperatures employed, is not nearly so much increased by increase in temperature as is the formation reaction.

It can be seen from the experiments plotted in Fig. 2 and from experiments 24, 35 and 40 plotted in Fig. 3 that the rate of formation of ammonium chloride in the pre-break region increases with increase of temperature from an almost negligible value at −75° in comparison with the rate in the post-break region until at −38° it equals about 10% of the post-break rate. Thus the considerable difference in temperature coefficients allows the decomposition reaction to be observed alone at lower temperatures.

Further, the fact that higher yields of hydrazine have been obtained at higher temperatures in liquid ammonia[9] can be explained by assuming a lower temperature coefficient for the decomposition reaction than for the formation reaction. Thus the yield studies agree with the kinetic studies.

(d) **The Effect of Concentration on Yields.**—It was reported by Sisler, Neth and Hurley[9] that higher yields of hydrazine are formed in liquid ammonia solutions at lower concentrations of chloramine. The explanation of this effect is that the concentration of the hydrazine formed will be low, also, and loss through the decomposition reaction, depending as it does on both concentrations, will be small. However, only one of the two reactants of the formation reaction is at low concentration, the chloramine.

The kinetic studies revealed the unsuspected additional reason for higher yields at lower concentrations: an induction period occurs in the decomposition reaction. Further, decreases in concentrations of chloramine and hydrazine lengthen the induction period. During the prolonged induction period in the more dilute solutions, the formation reaction proceeds so far that by the time the hydrazine is concentrated enough for the decomposition reaction to begin, the chloramine is so much spent that it cannot consume much of it. Hence loss by the decomposition reaction is restricted and yields are higher.

(e) **Factors Affecting the Length of the Induction Period.**—The induction period is lengthened by decreasing the concentration of the reactants, chloramine and hydrazine, as demonstrated by experiments 5 through 22 at −75° (Table II and Fig. 2). In some twenty-five experiments, not reported here, in which massive quantities of hydrazine were used, the experiments began with the decomposition reaction in full progress, so that the induction period could not be observed at all.

Near duplicate experiments exist in which the break occurs in one and not the other, as in the case of experiments 24 and 28 at −60°. This lack of reproducibility indicates that factors other than concentrations of known reactants are involved in determining the length of the induction period. They possibly include the presence of metal catalysts, variation in the water content of reagents and shift of the reaction from largely heterogeneous to largely homogeneous character depending on the surface condition of the reaction vessel.

The possibility that the break occurred because of contamination of the solution from metal ions derived from mercury pools in the electrode arms of the conductivity cell was eliminated by performing some experiments in a cell having mercury free electrode connections. These reactions, nonetheless, exhibited the characteristic break in rate (experiments 41 through 44 at −38°).

Experiments 14 through 18 at −75° were performed to demonstrate the effect of increasing ammonium chloride concentration on the length of the induction period. No correlation was observed. Possibly the effect was masked by random variations of more important factors.

(f) **Proposed Mechanism of the Decomposition Reaction.**—A free radical mechanism of the decomposition reaction is proposed to account for the several phenomena observed: (1) the stoichiometry, (2) the induction period, (3) the erratic variations in the induction period, (4) the effect of concentration on the induction period, (5) the high reaction rate and (6) the relative insensitivity to temperature change. The purely speculative nature of many of the details of this mechanism is appreciated, but the mechanism should provide a useful model for future tests.

(i) **Hydrazine Formation.**—The Bodenstein and Cahn and Powell mechanism is repeated here for convenience of reference

$$NH_3 + NH_2Cl \longrightarrow NH_2NH_3^+ + Cl^- \quad (28)$$

$$NH_2NH_3^+ + NH_3 \rightleftarrows NH_4^+ + NH_2NH_2 \quad (29)$$

(ii) **Triazane Formation.**—The intermediate, triazane, is thought to accumulate slowly by a reaction completely analogous to the formation reaction, equations 28 and 29

$$NH_2NH_2 + NH_2Cl \longrightarrow NH_2NH_2NH_2^+ + Cl^- \quad (30)$$

$$NH_2NH_2NH_2^+ + NH_3 \rightleftarrows NH_2NHNH_2 + NH_4^+ \quad (31)$$

Presumably the induction period is the time required to build up the triazane concentration to some initial value. The concentration of chloramine and hydrazine would decide the rate at which the intermediate was accumulated, and, hence, account for their effect on the length of the induction period.

(iii) **Chain Initiation.**—The chain carrier is postulated to be the amide radical, $NH_2\cdot$. The radical is relatively long lived since probable reactions it may undergo regenerate it

$$NH_2\cdot + NH_3 \longrightarrow NH_3 + NH_2\cdot \quad (32)$$

$$NH_2\cdot + NH_2Cl \longrightarrow NH_2Cl + NH_2\cdot \quad (33)$$

Chain initiation may occur as a homogeneous and/or surface catalyzed reaction of the intermediate, triazane

$$NH_2NHNH_2 \longrightarrow NH_2\cdot + NH_2NH\cdot \quad (34)$$

To account for the possible effect of metal ion catalysts which may initiate the chain reaction at variable times, depending on their concentrations, additional steps are included.

$$NH_2NH_2 + M^{+N} \longrightarrow NH_2\cdot + NH_2^+ + M^{+N-1} \quad (35)$$

$$NH_2NHNH_2 + M^{+N} \longrightarrow NH_2\cdot + N_2H_3^+ + M^{+N-1} \quad (36)$$

The effect of ammonium chloride on yields has led Drago and Sisler[17] to suggest that the decomposition of hydrazine may be acid catalyzed. Thus, a step is included in the mechanism which indicates that ammonium ion hastens chain initiation through shifting the equilibrium of equation 31 to the triazinium ion which then can initiate the chain reaction

$$NH_2NH_2NH_2^+ \longrightarrow NH_2NH_2^+ + NH_2\cdot \quad (37)$$

Though no correlation between length of induction period and ammonium chloride concentration was observed, it is possible that the over-all *rate* of the decomposition reaction is enhanced by the presence of ammonium chloride. Such an effect may be observable at higher concentrations since most yield studies were reported at higher concentrations.

(iv) **Chain Propagation.**—The free radical chain reaction is presumed to be carried by the amide radical, $NH_2\cdot$, which abstracts hydrogen from hydrazine

$$NH_2\cdot + NH_2NH_2 \longrightarrow NH_3 + \cdot NHNH_2 \quad (38)$$

The $NHNH_2\cdot$ radical abstracts chlorine from chloramine and regenerates the chain carrier, $NH_2\cdot$

$$NHNH_2 + ClNH_2 \longrightarrow ClNHNH_2 + NH_2\cdot \quad (39)$$

Ammonia removes the elements of hydrogen chloride leaving the diazene molecule

$$NH_3 + ClNHNH_2 \longrightarrow NH_4^+ + Cl^- + NH{=}NH \quad (40)$$

Chloramine oxidizes the diazene molecule to nitrogen

$$NH{=}NH + NH_2Cl \longrightarrow NH_4^+ + Cl^- + N_2 \quad (41)$$

The net effect of the chain propagation step is to effect the experimentally determined decomposition reaction, equation 2.

(v) **Chain Termination.**—Chain termination is effected through the combination of two of the chain carrying amide radicals

$$2NH_2\cdot \longrightarrow NH_2NH_2 \quad (42)$$

It should be noted that the nitrogen atoms originally contained in the hydrazine remained united in the chain propagation steps and form the end product, nitrogen. Exception is made of the atoms of nitrogen used to form triazane. These will be mixed in the products. If it is desired that this mechanism predict substantially no scrambling of nitrogen atoms in the process, it is only necessary to suppose that relatively few molecules of triazane are used in initiating the chains which are themselves of relatively great length. In any case, the nitrogen atoms of the chloramine molecules which are consumed in the chain propagation steps finally appear in ammonium chloride.

It is reported by Higginson and Sutton[21] as a result of studies using isotopically marked hydrazine that there is no scrambling of nitrogen in the oxidation of hydrazine observed in alkaline solution. The mechanism proposed here conforms to their experimental results if, as has already been suggested, the chains are thought to be long.

They and also Cahn and Powell[22] (following a similar technique) arrive at a mechanism which for the oxidation of hydrazine under these conditions leads from hydrazine by oxidation to the hydrazyl radical, $\cdot NHNH_2$. The latter is oxidized further to diazene, $NH{=}NH$, which suffers rapid oxidation to nitrogen. This mechanism also predicts no randomization of isotopic nitrogen but has the defect that it does not predict properties usually associated with chain reactions, such as the low temperature coefficient and the induction period found in the present work.

The three mechanisms proposed by Kirke and Browne[23] for the oxidation of hydrazine under most conditions are non-chain processes. They involve among them six hydrogen–nitrogen intermediates, including diazene, tetrazane and two tetrazenes. They do not predict the several extents of randomization of isotopic nitrogen observed by Cahn and Powell[22] using a variety of oxidizing agents at several acidities.

A number of attempts were made to find a simple relation between the concentrations of reactants and the observed rates of the decomposition reaction. The results were indecisive. Calculations were made to test the free radical chain mechanism proposed in equations 28 through 42. It was not found possible to correlate quantitatively the time for the inflection point in the rate data (Figs. 2 and 3) with the concentrations of the known reactants. A quantitative fit of all the data was not expected since some duplicate experiments gave greatly different induction periods.

However, in view of the large number of phenomena that the mechanism accounts for, it is thought that complications must result from partial heterogeneous character and/or metal catalyzed initiation of the reaction. The mechanism is, in general, consistent with the stoichiometry, the period of induction, the relatively large reaction rate, the temperature insensitivity and the lack of randomization of isotopic nitrogen associated with the decomposition reaction. Further tests of the mechanism of the decomposition reaction are in progress.

Extrapolation to the Water System.—The authors are aware that a considerable measure of extrapolation is necessary in order to extend conclusions based on reactions in liquid ammonia to those in water, and *vice versa*. Such extensions as have been made or inferred are hereby qualified for, as has been pointed out,[24] the reactions in liquid ammonia differ from those in water in several features: (a) the absence of the catalytic effect of trace metal ions to the extent that this effect is observed in water, (b) the absence of an effect of potassium amide on hydrazine yield, (c) the absence of any effect by gelatin and other inhibitors.

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[22] J. Cahn and R. Powell, THIS JOURNAL, **76**, 2568 (1954).

[23] R. E. Kirk and A. W. Browne, *ibid.*, **50**, 337 (1928).

[24] R. S. Drago, private communication.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Solvent Effect on a Primary Carbon Isotope Effect—Decarboxylation of Trinitrobenzoate Ion in Water and Ethanol-Water Mixture[1]

BY PETER RIESZ[2] AND JACOB BIGELEISEN

RECEIVED MAY 16, 1959

Carboxyl carbon, C^{12}-C^{13}, isotope effects have been determined for the decarboxylation of trinitrobenzoate ion in water and 90% ethanol between 30 and 80°. A small but significant difference is found in the isotope effects in the two solvents. The difference is correlated with solvation effects.

Introduction

The kinetics of decarboxylation of 2,4,6-trinitrobenzoic acid have been studied in ethanol[3] and in dioxane–water mixtures[4] by Verhoek and Trivich. The rate-determining step was shown to be the unimolecular decomposition of the trinitrobenzoate ion. The rate of decarboxylation was found to increase with decreasing dielectric constant of the

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] National Cancer Institute, National Institutes of Health, Bethesda 14, Maryland.

[3] F. H. Verhoek, THIS JOURNAL, **61**, 186 (1939).

[4] D. Trivich and F. H. Verhoek, *ibid.*, **65**, 1919 (1943).