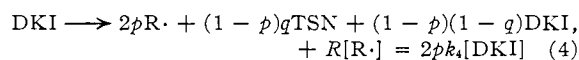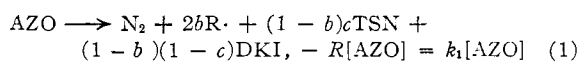# The Kinetics of the Thermal Decomposition of 2,2'-Azo-bis-isobutyronitrile[1a]

BY P. SMITH[1b] AND S. CARBONE

RECEIVED MARCH 28, 1959

The extent of formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine, DKI, and the first-order rate constants for the decomposition of DKI and 2,2'-azo-bis-isobutyronitrile, AZO, have been estimated from a kinetic study of the breakdown of AZO in benzene solution at 60–80°.

Introduction

The object of this work was to compare the extent of formation of DKI during the thermal decomposition of AZO with that found in a parallel study[2] of the photolysis of AZO in the same solvent at 25°. To this end the thermal breakdown of AZO was followed at 60–80° *via* the nitrogen evolution and spectrophotometric methods.[3] The mechanism of this reaction, neglecting formation of side products,[3] can be written

$$AZO \longrightarrow N_2 + 2bR\cdot + (1 - b)cTSN +$$
$$(1 - b)(1 - c)DKI, - R[AZO] = k_1[AZO] \quad (1)$$

$$2R\cdot \longrightarrow TSN, -R[R\cdot] = k_2[R\cdot]^2 \quad (2)$$

$$2R\cdot \longrightarrow DKI, -R[R\cdot] = k_3[R\cdot]^2 \quad (3)$$

$$DKI \longrightarrow 2pR\cdot + (1 - p)qTSN + (1 - p)(1 - q)DKI,$$
$$+ R[R\cdot] = 2pk_4[DKI] \quad (4)$$

where R· and TSN are the 2-cyano-2-propyl radical and tetramethylsuccinonitrile, respectively. Equations 1 and 4 give the net results of the primary breakdown, *via* free radical and molecular routes, of AZO and DKI, respectively. In each case the products are those that emerge from the reaction cage, taken to be the region of primary and geminate destruction processes, *e.g.*, of those AZO molecules that decompose in the primary act fractions b, $(1 - b)c$ and $(1 - b)(1 - c)$ appear as R·, TSN and DKI, respectively. To emphasize the possibility of cage recombination of R· radicals in (4), k_4 is defined in terms of the appearance rate of R· outside the natal cage. This was not done for (1) because cage reformation of AZO was assumed absent, *i.e.*, RN$_2$· radicals are absent or unimportant in (1). Step 1 and the rest of the mechanism could be readily modified to allow for other possibilities, if later work should justify them. If AZO and DKI break down in their respective primary steps solely *via* free radical paths and R· radicals within and outside the cages recombine in the same way, then c, q and $k_2/(k_2 + k_3)$ should be equal. This assumes, again, that RN$_2$· radicals are unimportant in (1)—a likely possibility.[4]

Applying the stationary state approximation to the concentration of R· outside the primary cages and making the plausible assumption that $k_1 \neq k_4(1 - (1 - p)(1 - q) - (pk_3)/(k_2 + k_3))$ gives

$$[DKI] = k_1 V[AZO]_0(e^{-k_1 t} - e^{-k_4 Ut})/(k_4 U - k_1) \quad (5)$$

$$(R[DKI])_0 = k_1 V[AZO]_0 \quad (6)$$

$$[DKI]_{max} = V[AZO]_0(k_1/(k_4 U)) \beta = V[AZO]_0 e^{-k_4 Ut_{max}} \quad (7)$$

$$(k_1 - k_4 U)t_{max} = \ln(k_1/(k_4 U)) \quad (8)$$

where U, V and β are $(1 - (1 - p)(1 - q) - (pk_3)/(k_2 + k_3))$, $((1 - b)(1 - c) + (bk_3)/(k_2 + k_3))$ and $k_4 U/(k_4 U - k_1)$, respectively.[5] Applying (8) to the previous experimental data available[3,6] indicates that $k_4 U/k_1$ is *ca.* 0.7–1.0 at 70–100° in toluene solution. This near equality of k_1 and $k_4 U$ was confirmed in the present investigation and used to give a way of estimating $k_4 U$ and V *via* the approximate equation

$$\ln([DKI]/t) = -(k_1 + k_4 U)t/2 + \ln(k_1 V[AZO]_0) \quad (9)$$

derivable from (5) providing certain conditions hold (see Appendix).

Experimental

Materials.—The AZO and the benzene were of similar quality to those used before for kinetic purposes.[2] The DKI was the same sample described previously.[2]

Apparatus and Procedure.—The reaction vessels were *ca.* 30 ml. Pyrex bulbs. They were each charged with a known mass of reaction mixture, then degassed and sealed off *in vacuo* in the usual way.[2] The nitrogen evolved by a reacted reaction mixture was extracted therefrom using a Toepler pump, after first freezing the reaction mixture with liquid nitrogen and cracking open the vessel. For effective nitrogen removal two series of extractions separated by a thaw period proved adequate. The extracted nitrogen then was measured using a calibrated Van Slyke–Neill manometer, Fischer Scientific Co. Cat. No. 6-409. Following the nitrogen extraction, reaction mixtures were thawed and examined at 5–10 mμ intervals over the 310–390 mμ range in 1 cm. quartz cells using a Beckman Model DU spectrophotometer, fitted with a type 4300 photomultiplier attachment and a thermojacketed cell compartment at 25.0°, operated at 0.042 mm. slit width and calibrated in the manner mentioned elsewhere.[2] The extinction coefficients of AZO and DKI in benzene solution were checked as being concentration independent for the molarity and wave length ranges of concern and in good agreement with those found previously using a Cary spectrophotometer.[2] All runs were carried out using vessels charged with *ca.* 10 ml. of reaction mixture 0.1000 *M* in AZO at 25.0° and immersed in a thermostat bath maintained at 59.98, 69.99 or 79.91 ± 0.02° (N.B.S. standard thermometers). Infinity readings by both methods of following the reaction confirmed expectation[2] that the nitrogen evolution is quantitative and the final reaction products are diactinic at 310–390 mμ. The results obtained at each temperature were dealt with as follows. The nitrometric data were plotted in a first-order manner *vs.* t_{obsd}, the duration of the immersion period of a reaction vessel in the bath, yielding a linear plot and hence estimates of k_1 and t_{cor}, the apparent time of the reaction start. They were used also to correct the observed optical

(1a) From the M.S. thesis of S. Carbone, Jan., 1959; presented at the 135th A.C.S. Meeting, Boston, Mass., and supported partly by a grant from E. I. du Pont de Nemours and Company. (1b) Chemistry Department, Duke University, Durham, N. C.

(2) P. Smith and A. M. Rosenberg, THIS JOURNAL, 81, 2037 (1959).

(3) M. Talât-Erben and S. Bywater, *ibid.*, 77, 3710, 3712 (1955); *Ricerca sci.*, Supplemento A, 25, 11 (1955).

(4) *E.g.*, S. G. Cohen and C. H. Wang, THIS JOURNAL, 77, 3628 (1955).

(5) If $k_1 = k_4 U$ (6) still holds and the corresponding equations to (5), (7) and (8) are $[DKI] = k_1 V[AZO]_0 t e^{-k_1 t}$, $[DKI]_{max} = V[AZO]_0/e$ and $k_1 t_{max} = 1$, respectively. It should be pointed out that $k_4 U$ is the first-order rate constant for DKI disappearance as conventionally defined.

(6) This was done graphically using the data in Table AII (see Appendix).

densities at 310–340 mμ for the contributions from unde-composed AZO. For each t_{obsd} value the plot of the corrected optical density, D^λ_c, vs. e^λ_{DKI} over the λ range 310–340 mμ was linear and provided an estimate of [DKI]. The graph of log ([DKI]/($t_{obsd} - t_{cor}$)) vs. t_{obsd}, following equation 9, was next made, its slope and the extrapolated value of log ([DKI]/($t_{obsd} - t_{cor}$)) for $t_{obsd} = t_{cor}$ gave estimates of ($k_1 + k_4U$)/2 and V, respectively. The use of the t_{cor} correction term, about 100 sec. and obtained by extrapolation of the nitrometric first-order plot, was particularly necessary for the data at 80° because of the short reaction times employed.

Results and Discussion

Typical of the results obtained are those il-lustrated in Figs. 1 and 2 relating to runs at 80°. Table I summarizes the data gained from all runs. The listed k_1 values tally as well as can be expected with the literature, the agreement being particularly close for the only strictly comparable result avail-able.[7] The log ([DKI]/($t_{obsd} - t_{cor}$)) vs. t_{obsd} plots were smooth straight lines in harmony with the results for $k_1/(k_4U)$ that may be computed from Table I and the fact that t_{obsd} in no case was allowed to > 1/k_1 (see Appendix). All the results for $k_1/$

TABLE I

SUMMARIZED RESULTS FROM ALL RUNS[a]

Temp., °C.	k_1	k_4U	V
80	1.44	1.59	0.567
70	0.399	0.445	.576
60	0.0994	0.117	.571

[a] The units of k_1 and k_4U are $10^{-4} \times$ sec.$^{-1}$; those of V, mole of DKI/mole of AZO. The estimated maximum un-certainties for k_1, k_4U and V are ca. $\pm$ 2.5, 7.5 and 6.0%, respectively. The k_4U data arise from the corresponding values of ($k_1 + k_4U$)/2 at 80, 70 and 60°, which are 1.51, 0.422 and 0.108 $\times$ 10^{-4} sec.$^{-1}$ (ca. $\pm$ 2.5%), respectively. Least square calculations were used throughout.

(k_4U) in this work do not agree very well with those deducible from the previous k_1t_{max} data available; e.g., at 70° this ratio is 0.88 $\pm$ 0.08 and 1.3$_5$ in this study and that of Talât-Erben and Bywater,[3] respectively. The earlier investigation was with toluene as solvent, a factor of possibly minor im-portance. The main source of difference is prob-ably the experimental difficulty[3] in estimating t_{max}. This view is supported by the published[3,8] plots of [DKI] vs. t for runs at 80°, which show maxima that are blunt shaped, suggesting that a precise estimate of t_{max} would require numerous [DKI] determinations around the maximum value. The data for V in Table I are similar to those pre-viously reported[3,8,9] for the reaction in toluene solu-

(7) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, 77, 3244 (1955), report one k_1 value for 62.5° in benzene solution obtained nitrometrically. J. P. Van Hook and A. V. Tobolsky, ibid., 80, 779 (1958), have estimated k_1 in benzene or toluene solution at 37–100° by the spectrophotometric method[3] at 360–380 mμ assuming DKI to be transparent. It is easy to show that this procedure should give k_1 estimates ca. 1–4% lower than the true values because DKI is not transparent in this region.[2] This deduction has been examined using our spectral data 360–380 mμ taken with the same solutions as were subjected to nitrogen evolution measurements, the k_1 results tending to bear out this view. The above discrepancies are, of course, similar in size to the scatter in the literature for data obtained by either method.

(8) M. Talât-Erben and A. N. Isfendiyaroğlu, Can. J. Chem., 36, 1156 (1958). In the case of ref. 3 the plots were actually of Dc^{120} vs. t.

(9) Apart from one rough[8] estimate of ca. 0.3 ref. 3 does not report any V values. However, columns 2, 4 and 5 and columns 2 and 3 of Table I therein indicate that at 70–100° e^{350}_{V} is 24 $\pm$ 2 and 17 $\pm$ 3, respectively. The 17 $\pm$ 3 value is probably the less reliable because it depends on initial rate data. The present work, using a different solvent and spectrophotometer, gives $e^{320}_{DKI}V$ as 24.3 $\pm$ 0.3 at 60–80°.
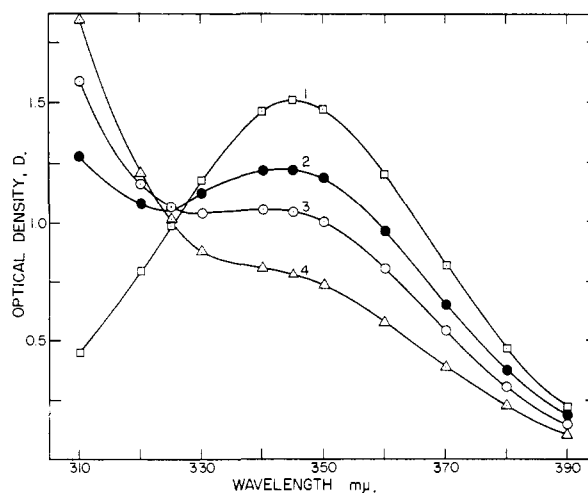
Fig. 1.—Variation of the optical density, D, with wave length, 310–390 mμ, and heating time, t_{obsd}, sec.: reaction temperature, 80°; [AZO]$_0$, 0.10 M, t_{obsd} values, 0, 1.8, 3.0 and 5.4 $\times$ 10^3 sec., respectively, for plots 1, 2, 3 and 4. Data taken at two other times are omitted for the sake of clarity.
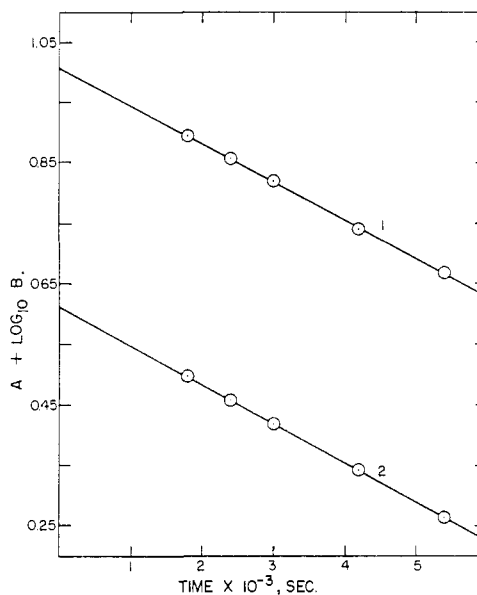

Fig. 2.—Variation of $A + \log B$ with heating time, t_{obsd}, sec.: reaction temperature, 80°; [AZO]$_0$, 0.10 M. For plots 1 and 2, respectively, A is 1.0 and 5.7, while B is ($P_\infty - P$)/P_∞ and [DKI]/($t_{obsd} - t_{cor}$) in M sec.$^{-1}$ units. The term t_{cor} is obtained from plot 1 by extrapolation of the straight line to give the value of t_{obsd} for which $A + \log B$ equals unity.

tion. They are also close to the corresponding results[2] for the photoreaction in the same sol-vent at 25°. This fact tends to confirm the idea[3] that DKI is formed from 2-cyano-2-propyl radicals by virtue of their ambident[10] character, rather than from RN$_2$· radicals, for example, which are less likely products of the photolytic primary

(10) A term previously coined to describe anions which can undergo covalent bond formation at either of two alternative sites; see N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, 77, 6269 (1955).

decomposition step than of the corresponding thermal primary act.[11] That $V > \frac{1}{2}$ is to be expected because cross coupling of R· radicals to form DKI should be favored over C–C coupling on three counts, viz., the operation of steric, polar and collisional statistical effects. Clearly, more extensive investigation of this and related systems is called for in order to assess the importance of these factors. Again, one would not expect ambident characteristics to be restricted to cyano free radicals, e.g., 2-nitro-2-propyl and 2-carboalkoxy-2-propyl[12] radicals appear likely to have this property also, by virtue of their $-NO_2$ and $>CO$ groups, respectively. It seems reasonable to expect R· radicals to form some dimethylketenazine, $(CH_3)_2C=C=N-N=C=C(CH_3)_2$, via N–N coupling as well as TSN and DKI. The fact that none has been found may be because it is unstable under the employed reaction conditions.

Appendix

Derivation of Equation 9.—Equation 5 may be written

$$k_4Ut + \ln \left([DKI]/(k_1V[AZO]_0t) \right) = \ln (1 + y) \quad (A1)$$

where $(1 + y) = (e^x - 1)/x$ and $x = (k_4U - k_1)t$. Assuming $|y| < 1$ and expanding $\ln (1 + y)$ in the usual convergent series gives

$$\ln (1 + y) = x/2 + x^2/24 - x^4/2880 \ldots \quad (A2)$$

the coefficients of x^3 and x^5 being zero. The function $x/(e^x - 1)$ has been tabulated,[13] from which it may be deduced that $0 \geqslant y \leqslant 1$ if $0 \leqslant x \leqslant 1.255$. Negative x values are of concern also. Should x be negative and put equal to $-x'$, it may be shown readily in the manner outlined above that providing $0 \leqslant x' \leqslant 1.255$

$$\ln ((e^{x'} - 1)/x') = (x')/2 + (x')^2/24 - (x')^4/2880 \ldots \quad (A3)$$

It is useful to consider the case when x is positive first. Equation A2 suggests that for small enough x values $\ln (1 + y) \doteq x/2 + x^2/24$. The validity of this assumption is illustrated in Table AI. The most useful range of x values is shown later to be $0 \leqslant x \leqslant ca. 1.1$ (see Table AII). Here the compared quantities differ by $\not> 0.083\%$. However, for all cited x values, $0 \leqslant x \leqslant 5.0$

$$x/2 < \ln (1 + y) < (x/2 + x^2/24) \quad (A4)$$

except in the limiting case $x = 0 = \ln (1 + y)$. These conclusions clearly hold whether the series in (A2) is convergent or not. From (A1) and (A4) it follows that

$$\ln ([DKI]/t) = x/2 + x^2/24 - w - k_1Ut + \ln (k_1V[AZO]_0) \quad (A5)$$

where $0 \leqslant w < x^2/24$. Equation A5 yields (9) providing $(x^2/24 - w) << |(x/2 - k_4Ut)|$, which can be restated as $(x^2/24 - w) \leqslant 0.005|(x/2 - k_4Ut)|$ or, as a safe approximation

$$x^2/24 \leqslant 0.005 (x/2 + k_1t) \quad (A6)$$

The maximum values of k_1t, denoted by k_1t^*, that satisfy (A6) for a series of $k_1/(k_4U)$ values are given in Table AII. Also presented are the corresponding data for k_1t_{max} and k_4Ut_{max}. Although (A6) does not strictly apply for $k_1 = k_4U$, inasmuch as (A1) assumes otherwise, it can be used to show that $k_1t^* \rightarrow \infty$ as $k_1 \rightarrow k_4U$. This case is included in Table AII. It can be also derived directly without approximation from the equation[5] corresponding to (5) for when $k_1 = k_4U$. If $x = -x_1 \leqslant 0$ the above treatment may be repeated to show that (9) holds if

$$(x')^2/24 \leqslant 0.005 ((x')/2 + k_1t) \quad (A7)$$

TABLE AI

COMPARISON OF $\ln ((e^x - 1)/x)$ AND $(x + x^2/12)/2$

x	$\ln((e^x - 1)/x)^a$	$(x + x^2/12)/2$
0.0	0.000,000	0.000,000
.1	.050,417	.050,417
.2	.101,666	.101,667
.3	.153,747	.153,750
.4	.206,658	.206,667
.5	.260,395	.260,417
.6	.314,955	.315,000
.7	.370,334	.370,417
.8	.426,526	.426,667
.9	.483,525	.483,750
1.0	.541,324	.541,667
1.1	.599,92	.600,42
1.2	.659,30	.660,00
1.3	.719,45	.720,42
1.4	.780,37	.781,67
1.5	.842,05	.843,75
2.0	1.161,44	1.166,67
3.0	1.850,3	1.875,0
4.0	2.595	2.667
5.0	3.38	3.54

^{a} Obtained from ref. 13 and by linear interpolation of the data in "Table of Natural Logarithms for Arguments between Zero and Five to Sixteen Decimal Places," Applied Mathematics Series 31, National Bureau of Standards, Washington, D. C., 1953.

TABLE AII

DATA ILLUSTRATING THE APPLICATION OF (A6) AND (A7)

$k_1/(k_4U)^a$	1.000	0.900	0.800	0.700	0.600	0.500	$k_4U/k_1{}^b$
k_1t^*	∞	10.260	2.160	.793	.360	.180	$k_1t'^*$
k_1t_{max}	1.000	0.949	0.893	.832	.766	.693	k_4Ut_{max}
k_4Ut_{max}	1.000	1.055	1.116	1.189	1.277	1.386	k_1t_{max}

^{a} $x \geqslant 0$. ^{b} $x' \geqslant 0$.

(11) The argument implied here is like that to which ref. 17 of our previous paper[2] is appended. It rests on the plausible assumptions that RN_2· radicals would not be expected to form DKI and TSN in the same ratio as R· radicals and that the excess energy available to R· and RN_2· radicals generated photolytically would be unlikely to confer on them different coupling properties; see also J. C. Bevington and T. D. Lewis, Trans. Faraday Soc., 54, 1340 (1958).

(12) J. S. Mackie and S. Bywater, Can. J. Chem., 35, 570 (1957), give some tentative evidence for this view in the case of 2-carbomethoxy-2-propyl radicals.

(13) J. Sherman and R. B. Ewell, J. Phys. Chem., 46, 641 (1942); G. J. Janz, "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press, Inc., New York, N. Y., 1958, pp. 139–154.

analyses are possibly not very accurate (e.g., for expt. 10 and 18 ($[TSN]_\infty + 2[IBN]_\infty)/[AZO]_0$ 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 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 $[IBN]_\infty/[TSN]_\infty$ 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

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

RECEIVED NOVEMBER 22, 1958

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.

$$NH_2Cl + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl \qquad (1)$$
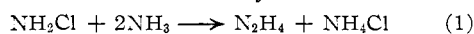
Yields in this process are reduced by a hydrazine consuming side reaction for which the following equation is proposed

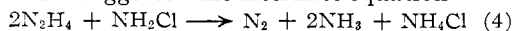$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl \qquad (2)$$

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

$$3NH_2Cl + 3OH^- \longrightarrow N_2 + NH_3 + 3Cl^- + 3H_2O \qquad (3)$$
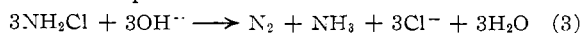
Joyner[5] suggested that the decomposition of ammonia by chloramine in the Raschig process probably passed through the intermediate hydrazine, and that the latter was oxidized in accordance with equation 2.

Laitinen[6] suggested the alternate equation

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

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.

(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).