

[CONTRIBUTION FROM YERKES RESEARCH LABORATORY, FILM DEPARTMENT, E. I. DU PONT DE NEMOURS AND Co., INC., BUFFALO, N. Y.]

Chemistry of 2,2'-Azobisisobutyramidine Hydrochloride in Aqueous Solution: A Water-soluble Azo Initiator¹

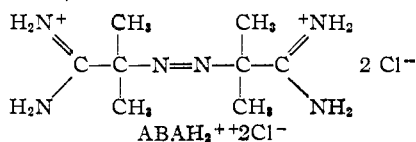
By THOMAS J. DOUGHERTY

RECEIVED APRIL 8, 1961

Thermal decomposition of 2,2'-azobisisobutyramidine hydrochloride ($\text{ABAH}_2^{++}2\text{Cl}^-$) in water has been shown to yield initially the product of free radical coupling, tetramethylsuccinamide hydrochloride (I), which undergoes cyclization to tetramethylsuccinimidine hydrochloride (II). Hydrolysis of the imidine to 2,2,3-trimethyl-3-guanylbutyramide hydrochloride (III), tetramethyl-5-imino-2-pyrrolidone (IV), and tetramethylsuccinimide (V) has been observed. The possibility of tetramethylsuccinimidine hydrochloride in the conjugated tautomeric form (IIa) as an intermediate is discussed.

Introduction

There are several advantages in the use of water-soluble, charged azo initiators for polymerization reactions. While the salts of 2,2'-azobisisobutyramidine² offer the desired combination of labile azo function and water solubility, the amidine moieties introduce the possibility of several side products which may be undesirable in the polymerization process and/or in the resulting polymers. A study was thus undertaken to elucidate the chemistry of 2,2'-azobisisobutyramidine hydrochloride ($\text{ABAH}_2^{++}2\text{Cl}^-$) under conditions similar to aqueous phase polymerization (excluding monomer).



Results

Kinetic Data.—To determine if the amidine functions were undergoing reaction at a rate comparable to decomposition of azo, rate constants for both reactions were measured at several temperatures in demineralized, deoxygenated water. The reactions followed simple first-order kinetics. Table I summarizes the results.

TABLE I
KINETIC DATA FOR LOSS OF AZO AND LOSS OF AMIDINE

T, °C.	Azo loss ^a $k \times 10^4$, min. ⁻¹	Amidine loss ^b $k \times 10^4$, min. ⁻¹
40.15	..	1.5
50.05	5.8	5.9
60.20	24.4	24.3
70.10	92.7	91.3
100.10	2990	...
ΔH^\ddagger , kcal./mole	29.1	29.3
ΔS^\ddagger , e.u.	+8.5	+9.2

^a In all runs equimolar or 100% mole excess HCl was added. Rate constants were independent of amount of added acid. ^b The actual rate of amidine loss is twice that of azo since there are two amidine functions per molecule. ^c Rate constants are averages of two or more runs.

Disappearance of the azo absorption in the ultraviolet at 365 $m\mu$ afforded a convenient means for following the rate of azo decomposition but was complicated by the appearance of an interfering

(1) Presented before the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, Abstracts, p. 17-O.

(2) For a discussion of the syntheses of these compounds and their use in polymerization, see R. W. Upson, U. S. Patent 2,599,299 (1952).

species absorbing at 292.5 $m\mu$. Addition of hydrochloric acid completely retarded the formation of this adsorption without affecting the rate of azo loss (Table I).

The rate of amidine consumption was followed iodometrically by application of a procedure developed by Stevens for quantitative analysis of certain aromatic amidines³ (see Experimental).

In the absence of added acid the change in absorption at 292.5 $m\mu$ with time could be followed (Fig. 1). The initial slope is concentration dependent, but the position of the maximum (approximately 300 min.) is concentration independent at 60°. The short induction period was shown not to be a result of radical scavenging by oxygen by carrying out the reactions in a carefully deoxygenated system. Deliberate addition of air tended to lengthen the induction period somewhat but not appreciably affect the remainder of the curve.

Product Identification.—Product isolation was carried out under various conditions. Refluxing aqueous $\text{ABAH}_2^{++}2\text{Cl}^-$ for 3.5 days resulted in a 60% yield of tetramethylsuccinimide V, (identified by elemental analysis, m.p. and infrared).

Heating a solution of $\text{ABAH}_2^{++}2\text{Cl}^-$ for one hour on a steam-bath gave a 45% yield of 2,2,3-trimethyl-3-guanylbutyramide hydrochloride III, (identified by elemental analysis, infrared and formation of tetramethylsuccinimide upon hydrolysis under neutral or basic conditions).

Partial decomposition by heating an aqueous solution of $\text{ABAH}_2^{++}2\text{Cl}^-$ in a constant temperature bath at 60° for 300 minutes (approximate half-life for azo loss) permitted isolation of several products. Continuous ether extraction yielded trace amounts of tetramethylsuccinimide (V). Removal of the water under vacuum followed by continuous chloroform extraction of the resulting solids (4 days) yielded three fractions⁴: a chloroform non-extractable fraction (80% of total) consisting of unreacted $\text{ABAH}_2^{++}2\text{Cl}^-$, the amidine salt III, and ammonium chloride; a slightly chloroform-soluble mixture (17%) which separated as an oil, consisting of III which slowly crystallized out upon standing⁵ and the intermediate as shown by absorption at 292.5 $m\mu$ ⁶; and

(3) F. H. Stevens, *Anal. Chem.*, **24**, 180 (1952).

(4) This procedure was first carried out by W. R. Hendrix of this department.

(5) Since III is very slowly extracted by chloroform, the actual amount in the oil depends upon the length of time of the extraction.

(6) An approximation of the rate of disappearance of the intermediate in water was determined spectrophotometrically using this oil. The reaction is first order with $k_{450} = 3.0\text{--}4.0 \times 10^{-3}$ min.⁻¹.

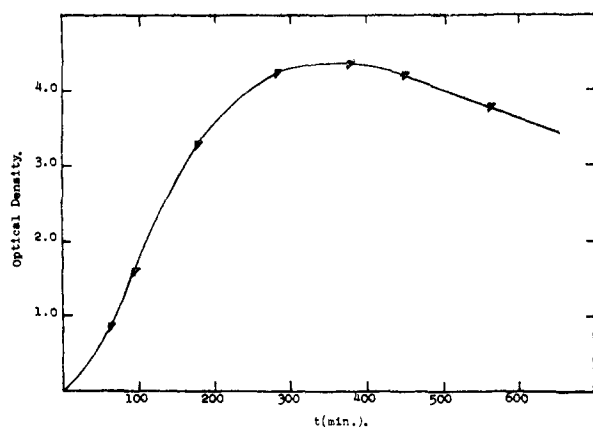
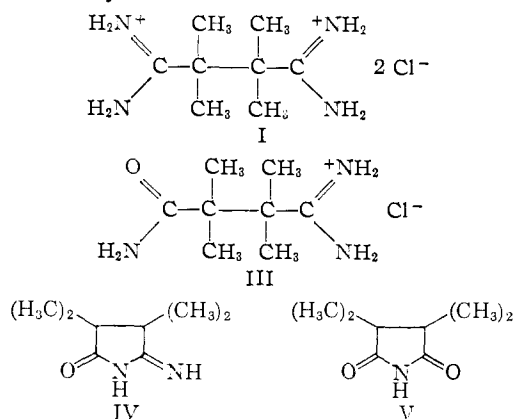
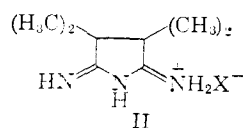


Fig. 1.—Rate of change of optical density at 292.5 $m\mu$.
 $T = 60.2^\circ$, $[ABAH_2^{++}2Cl^-]_0 = 0.0103 M$.

the third fraction, a chloroform-soluble material (trace) identified as tetramethyl-5-imino-2-pyrrolidone (IV) by elemental analysis, infrared and hydrolysis to tetramethylsuccinimide under neutral or basic conditions. Tetramethylsuccinimide hydrochloride (I) is probably a constituent of the chloroform-insoluble material (and/or the slightly chloroform-soluble oil) although it was not specifically identified. No products resulting from disproportionation were found, although minor amounts may be formed.



Tetramethyl-5-imino-2-pyrrolidone (IV) was obtained in greater amounts from a saturated aqueous solution of $ABAH_2^{++}2Cl^-$ which had been exposed to sunlight for approximately six months (see Experimental).



Tetramethylsuccinimide nitrate (II, $X = NO_3^-$) has been shown to be a product from thermal decomposition of $ABAH_2^{++}2NO_3^-$ in anhydrous dimethyl sulfoxide by Hammond and Neuman.^{7a} When a sample^{7b} of this compound was allowed to stand several days in water at room temperature, 2,2,3-trimethyl-3-guanylbutyramide hydrochloride (III) was isolated as the picrate (m.p.

(7) (a) G. S. Hammond and R. C. Neuman, Jr., private communication. (b) The author is indebted to these workers for this sample of the imidine nitrate.

and infrared identical to that of picrate from authentic III) indicating that hydrolysis may proceed by ring opening.

A sample of tetramethylsuccinimide nitrate^{7b} examined in this Laboratory showed a maximum in water at 292.5 $m\mu$ with ϵ 101. The magnitude of absorption in this region, however, was found to be pH sensitive as expected on the basis of its absence during kinetic runs in acid solution. When a $2.03 \times 10^{-3} M$ solution of the imidine nitrate in dimethyl sulfoxide (λ_{max}^{DMSO} 302.5 $m\mu$, ϵ 258)⁸ was acidified with aqueous hydrochloric acid to an extent of $2 \times 10^{-4} N$, the optical density slowly decreased from an initial value of 0.525 to 0.358 in 18 hours. Further acidification of this solution to a concentration of 0.2 N resulted in a drop of optical density to 0.02 in 8 minutes.

When a solution of approximately the same concentration in anhydrous dimethyl sulfoxide was strongly acidified ($\sim 0.1 N$ in acid) with anhydrous hydrogen chloride, the optical density decreased to a constant low value (~ 0.05) in 10 minutes.

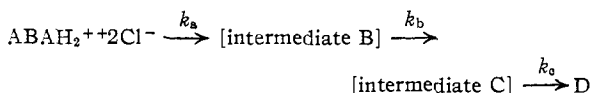
A solution of the imidine nitrate in ethanol (λ_{max}^{EtOH} 298 $m\mu$) which was acidified to 0.2 N with 70% nitric acid resulted in almost complete loss of absorption after 10 minutes. The material isolated after 30 minutes (>90%) had an infrared spectrum essentially unchanged from that of the starting imidine nitrate with the exception of the presence of a weak band at 9.2 μ . When a similarly acidified solution remained overnight, the isolated material had an infrared spectrum very different from the imidine nitrate (see Experimental).

After 20 hours the optical density of a solution of the imidine nitrate in absolute ethanol had dropped to approximately 70% of its original value.

Discussion

The kinetic data (Table I) indicate that both loss of azo and loss of amidine are occurring with the same rate-controlling process; rate constants and thermodynamic parameters are identical within experimental error for both reactions. The relatively large enthalpy of activation (~ 29 kcal./mole) and favorable entropy of activation (+8–9 e.u.) are indicative of a chain-scission process such as decomposition of azo compounds. These values may be compared with an enthalpy of activation of 31 kcal./mole and an entropy of activation of +11.7 e.u. for decomposition of 2,2'-azobisisobutyronitrile in benzene.⁹ It thus appears that the amidine functions are consumed in a fast step subsequent to rate-determining azo decomposition.

The type of behavior noted for the material with $\lambda_{max}^{H_2O}$ 292.5 $m\mu$ (Fig. 1) is characteristic of an intermediate (C) whose precursor is itself an intermediate (B).



(8) This sample was prepared in this Laboratory by a procedure similar to Hammond and Neuman (see Experimental).

(9) Calculated from data of P. Smith and S. Carbone, *J. Am. Chem. Soc.*, **81**, 6174 (1959).

The kinetic expression for C is given by eq. 1 which integrates to eq. 2.¹⁰

$$\frac{dc}{dt} = \frac{k_a k_b [A]_0}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) - k_c [C] \quad (1)$$

$$[C] = \frac{k_a k_b [A]_0}{k_b - k_a} [(k_a - k_b) e^{-k_c t} + (k_a - k_b) e^{-k_a t} - (k_c - k_a) e^{-k_b t}] \quad (2)$$

where [C] is the concentration of intermediate C at time t and $[A]_0$ is the initial concentration of $\text{ABAH}_2^{++} + 2\text{Cl}^-$.

The short induction period indicates that while $k_b > k_a$, it is not sufficiently different to allow the concentration of B to be treated by the steady-state approximation. A curve calculated according to eq. 2, which has the same form as the experimental curve (Fig. 1), is obtained using values obtained at 60° for k_a (Table I) and k_c of $2.44 \times 10^{-3} \text{ min.}^{-1}$ and $4.0 \times 10^{-3} \text{ min.}^{-1}$ respectively, and setting $k_b = 2.4 \times 10^{-2} \text{ min.}^{-1}$.

The concentration of C at the maximum may be estimated from eq. 3 (obtained from eq. 1 by setting

$$[C]_{\text{max}} = \frac{k_a k_b [A]_0}{k_c (k_b - k_a)} (e^{-k_a t} - e^{-k_b t}) \quad (3)$$

$dc/dt = 0$). Setting $[A]_0 = 0.0103$ (Fig. 1) and using the above values for rate constants, $[C]_{\text{max}} = 3.34 \times 10^{-3} M$. Assuming adherence to Beer's law and using the value of 4.2¹¹ for the optical density corresponding to $[C]_{\text{max}}$ (Fig. 1), $\epsilon = 1260$. Since ϵ at 292.5 $m\mu$ for the sample of tetramethylsuccinimidine nitrate obtained from Hammond and Neuman^{7b} was 101, it may be estimated that the material exhibiting this absorption constitutes a maximum of 8% of the sample and that the sample obtained in this Laboratory³ a maximum of 20% ($\epsilon = 258$).¹²

Two structures for the intermediate may be considered based upon its ultraviolet spectrum. Dimethyl-N-(2-guanyl-2-propyl)-ketenimine hydrochloride (VIII) could be formed as a result of carbon to nitrogen coupling of radicals¹³ according to Chart I.

Since product isolation was not quantitative, failure to observe the hydrolysis product of VII, dimethyl-N-(2-guanyl-2-propyl)-isobutyramide hydrochloride (VIII)¹⁴ or cyano-containing compounds resulting from homolytic cleavage,¹³ does not rule out the mode of decomposition as outlined in Chart I.

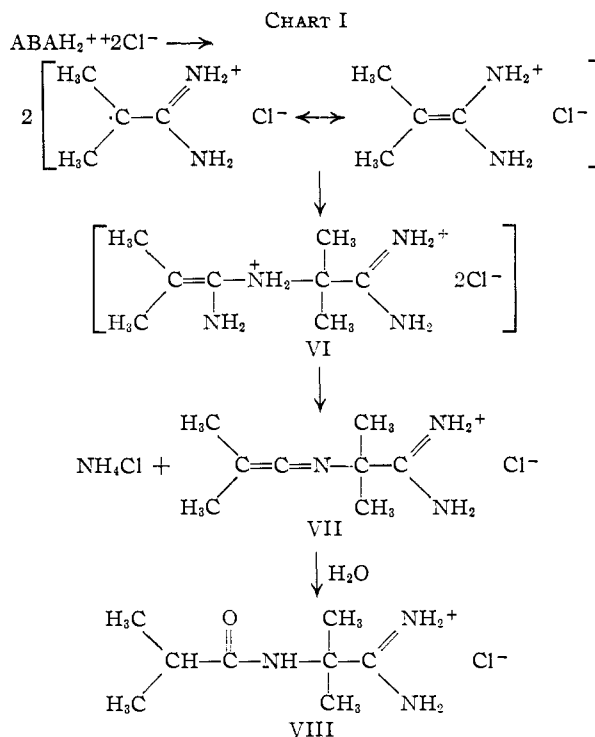
(10) These equations are derived similarly to eq. 15; A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 154, with the exception that C is not a stable product.

(11) This value was obtained by multiplication of the optical density of diluted samples by the dilution factor.

(12) Equations 1-3 assume that the reaction proceeds entirely through the intermediate leading to a maximum value of $[C]_{\text{max}}$ and a minimum value for ϵ . The concentrations of the intermediate in these samples may thus be much less than estimated.

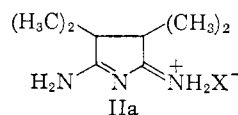
(13) Dimethyl-N-(2-cyano-2-propyl)-ketenimine, $[\lambda_{\text{max}}^{\text{benzene}} 291 m\mu, \epsilon 150.5$; P. Smith and M. Rosenberg, *J. Am. Chem. Soc.*, **81**, 2037 (1959)] is an intermediate in decomposition of 2,2'-azobisisobutyronitrile in non-aqueous solution. This ketenimine may break down to re-form 2-cyano-2-propyl radicals [M. Talât-Erben and S. Bywater, *ibid.*, **77**, 3710, 3712 (1955)].

(14) Certain phenyl-substituted ketenimines are relatively stable in neutral solution but rapidly hydrolyzed to the corresponding amides by acid; H. Staudinger and J. Meyer, *Ber.*, **53**, 62 (1920), and C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657 (1953);

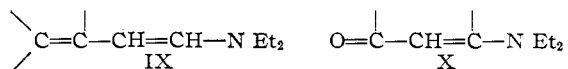


The ketenimine structure however may be ruled unlikely on the basis of the estimated extinction coefficient at 292.5 $m\mu$ for the intermediate. The value of 1260 is an order of magnitude greater than the extinction coefficient of 150 at 291 $m\mu$ measured for essentially pure dimethyl-N-(2-cyano-2-propyl)-ketenimine.^{13,15}

A second structure to be considered is the conjugated tautomer of tetramethylsuccinimidine hy-



drochloride (IIa, X = Cl⁻). Elvidge and Linstead¹⁶ have pointed out that structures of type IIa would be expected to absorb in the 300 $m\mu$ region by analogy with compounds of type IX and X which show high intensity absorption between 280-300 $m\mu$.^{17,13}



Although tautomeric forms such as IIa have not to date been shown to exist in equilibrium with the diimino forms such as II, Elvidge and Linstead observed that the fine structure of N,N'-diphenylsuccinimidine hydrochloride hemihydrate in the ultraviolet shows a maximum at 312 $m\mu$ in methanol ($\epsilon 23,000$) indicating that there may be some contribution from the conjugated form corresponding to IIa.

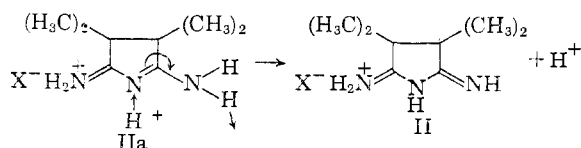
(15) A similar extinction coefficient would be expected for ketenimine VII.

(16) J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 442 (1954).

(17) E. A. Braude, *Ann. Repts.*, **42**, 105 (1945), and *J. Chem. Soc.*, 45 (1946).

(18) Substitution of nitrogen for carbon has little effect on the position of maximum absorption in 1,3-diene systems (H. C. Barany, E. A. Braude and M. Pranha, *ibid.*, 1898 (1949)).

If absorption in the 300 $m\mu$ region is due to the conjugated tautomer IIa, it is interesting to speculate on the acid-catalyzed reactions. In aqueous solutions this may simply involve acid-catalyzed hydrolysis.¹⁹ In non-aqueous solution, however, the disappearance of absorption near 300 $m\mu$ may result from acid-catalyzed isomerization of form IIa to form II.



This postulate implies however that rapid proton exchange (as expected at least in aqueous solutions) should lead to rapid isomerization. Therefore, it would not be expected that the intermediate would be sufficiently long lived to be observed in kinetic measurements.

Recent work has shown that rates of proton exchange of salts of ammonia, methylamine and trimethylamine may become quite slow in very acidic solution.²⁰ The imidine salts may be representative of systems showing relatively slow rates of proton exchange even in neutral or slightly acidic solution.

An over-all scheme consistent with product identification and kinetic data is shown in Chart II (dotted lines represent uncertain reaction paths). Although the diamidine salt I, may or may not be a sufficiently short-lived intermediate to allow neglect of its rate in the rate expression for loss of amidine (which occurs upon cyclization to imidine II^{21,22}), it is likely that it would appear to be so as a result of the particular method employed for determining amidine (see Experimental). Thus, the amide-amidine III, does not analyze for amidine according to the method used in kinetic determinations perhaps as a result of excessive steric crowding around the amidine function. Arguing by analogy it would be expected that the diamidine I, in which the amidine functions are similarly crowded, would also fail to give the amidine test by this method. It would appear therefore that amidine had been consumed upon radical coupling to I (a very rapid step), leading to a rate constant for amidine loss identical to that for azo decomposition.²³

Experimental²⁴

2,2'-Azobisisobutyramidine hydrochloride ($ABAH_2^{++} \cdot 2Cl^-$), prepared by addition of ammonia to the imino ether of 2,2'-azobisisobutyronitrile according to reference 2, was

(19) An uncatalyzed hydrolysis may account for consumption of intermediate observed in kinetic measurements (Fig. 1).

(20) M. T. Emerson, E. Grunwald, M. L. Kaplan and R. A. Kromhout, *J. Am. Chem. Soc.*, **82**, 6307 (1960). Mean lives of the N-H covalent bond in NH_4^+ ranged from 0.16 sec. in dilute, slightly acidic solution to 15 hr. in 69.38% H_2SO_4 .

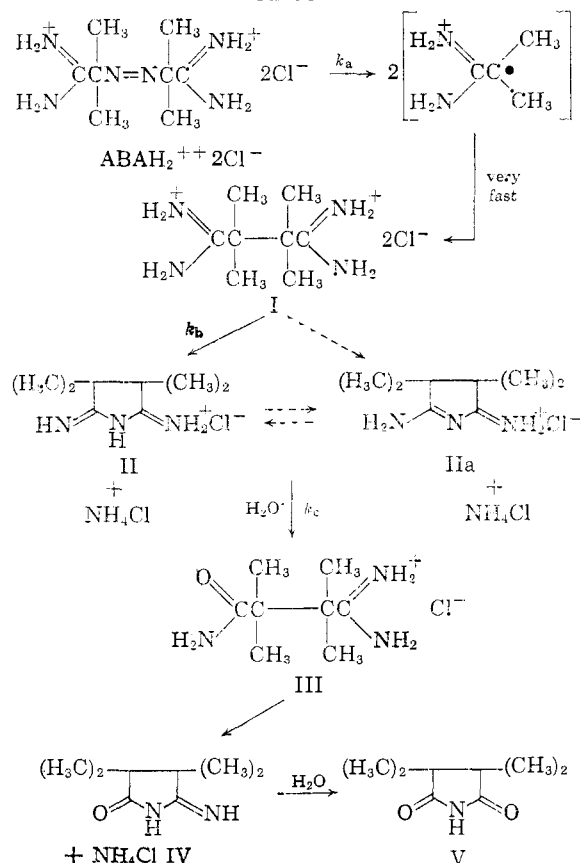
(21) Cyclization to succinimidine hydrochloride occurs upon dissolution of succinamide hydrochloride in water. A. Pinner, "Die Imidoäther und ihre Derivate," Oppenheim, Berlin, 1892.

(22) If this cyclization is not very rapid, its rate should appear in the rate expression for loss of amidine but not of course in that for azo decomposition.

(23) The kinetics for amidine loss show no evidence of different rates for the two functions up to 75% reaction. While this is not definitive it is consistent with the mechanism shown.

(24) All melting points are uncorrected. Elemental analyses by Schwarzkopf Laboratories, Woodside, N. Y.

CHART II



recrystallized by preparing a saturated solution in water at room temperature and storing several hours at 3°.

Kinetic solvent, demineralized, deoxygenated water was prepared by passing tap water through a commercial ion exchange resin and bubbling in nitrogen.

Kinetic Methods.—Azo loss was determined by following the change in optical density at 365 $m\mu$ (Beckman model DU spectrophotometer) of $ABAH_2^{++} \cdot 2Cl^-$ in solutions of the kinetic solvent (0.02 to 0.10 *M*) in the presence of equimolar of 100% mole excess of hydrochloric acid. The rate was independent of the amount of added acid. Individual samples of 2 to 4 ml. in capped polypropylene test-tubes were used. Linearity of optical density with concentration of $ABAH_2^{++} \cdot 2Cl^-$ was demonstrated. Since in the presence of acid none of the products absorb in the 250–400 $m\mu$ region, the final optical density was taken as zero. Plots of log optical density vs. time gave straight lines to 90% reaction. Substitution of distilled water for demineralized, deoxygenated water had little effect on the rates of azo loss. Rate constants at 50.05, 60.2, 70.1 and 100.1° were calculated from the slopes of the best straight lines drawn visually through the experimental points (Table I).

Thermodynamic parameters of activation, ΔH^\ddagger and ΔS^\ddagger , were calculated from the Eyring equation.²⁵

Amidine disappearance was followed iodometrically.⁸ A typical run consisted of withdrawing individual 2-ml. (room temperature volume) samples of $ABAH_2^{++} \cdot 2Cl^-$ solution (0.05 to 0.11 *M* in kinetic solvent) in polypropylene test-tubes, cooling rapidly in a stream of cold water, adding to excess standard iodine solution followed immediately by excess 2 *N* sodium hydroxide solution. After stirring 5 to 10 minutes²⁶ the fine yellow precipitate of iodoamidine was filtered off, washed several times with distilled water, the combined filtrate and washings acidified with 4*N* hydrochloric acid and excess iodine titrated with standard sodium thiosulfate solution. The analytical method was checked by determining known amounts of $ABAH_2^{++} \cdot 2Cl^-$.

(25) A. A. Frost and R. G. Pearson, ref. 10, p. 96, eq. 49.

(26) If stirring was continued much longer than 10 minutes, the precipitate turned dark and erratic results were obtained.

Plots of $\log [\text{ABAH}_2^{++}2\text{Cl}^-]$ versus time gave straight lines to 75% reaction. Rate constants were determined at 40.0°, 50.05°, 60.2°, 70.1° and are the average of at least two runs (Table I).

The rate of change of optical density of the intermediate ($\lambda_{\text{max}}^{292.5}$ 292.5 μ) was followed spectrophotometrically at 60.2° as described for azo loss with the exception that no acid was added and initial $\text{ABAH}_2^{++}2\text{Cl}^-$ concentrations were in the range 0.005–0.010 *M*. In addition to using deoxygenated demineralized water, the test-tubes were flushed with nitrogen before capping. Plots of optical density versus time gave curves with initial slopes dependent upon $[\text{ABAH}_2^{++}2\text{Cl}^-]_0$ and maxima at approximately 300 minutes (Fig. 1).

The constant temperature bath used in all runs regulated at $\pm 0.05^\circ$. The spreads of rate constants are approximately $\pm 5\%$ from the means.

Decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ to form 2,2,3-trimethyl-3-guanylbutyramide hydrochloride (III) was carried out by dissolving $\text{ABAH}_2^{++}2\text{Cl}^-$ (5.28 g., 1.95×10^{-2} mole) in 100 ml. of distilled water and heating 1 hour on a steam-bath. The solution was cooled, the water partially removed *in vacuo*, and stored overnight at 3°. The white crystalline precipitate amounted to 0.74 g. An additional 1.08 g. was obtained by further concentration *in vacuo* and cooling for a total yield of 45%. This yield is a minimum value since evaporation of the remaining water gave a mixture of ammonium chloride and III. The compound was recrystallized from ethanol-ether or water, m.p. $>300^\circ$. Ionic chloride was indicated with silver nitrate solution. The infrared spectrum showed NH at 2.89 μ and bands at 5.90-(m) and 6.10(s) μ .

Hydrolysis of this salt in refluxing water (2 days) gave tetramethylsuccinimide (by ether extraction) in 40% yield (m.p. 188–189°, sublimed,²⁷ characteristic carbonyl bands at 5.80 and 5.85–5.90 μ). On this basis, the compound is assigned the structure 2,2,3-trimethyl-3-guanylbutyramide hydrochloride (III).

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{N}_3\text{ClO}$: C, 46.4; H, 8.8; N, 20.3; O, 7.7; Cl, 17.1. Found: C, 46.3; H, 8.6; N, 20.3; O, 7.8; Cl, 16.9. The picrate has m.p. 262–265°.

Decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ to form tetramethylsuccinimide was accomplished by dissolving $\text{ABAH}_2^{++}2\text{Cl}^-$ (10.0 g., 3.69×10^{-2} mole) in 100 ml. of distilled water and refluxing 3.5 days. The solution was cooled, partially concentrated *in vacuo* and stored several hours at 3° to yield 2.17 g. of tetramethylsuccinimide. An additional 1.25 g. was obtained by extracting with ether to give a total yield of 60%.

Decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ to 50% reaction was effected by dissolving $\text{ABAH}_2^{++}2\text{Cl}^-$ (10.0 g., 3.69×10^{-2} mole) in distilled water and maintaining at 60° for 300 minutes (approximate half-life for azo loss). The solution was cooled and extracted continuously with ether for 5 days to yield 0.1 g. of tetramethylsuccinimide. The aqueous solution was evaporated to dryness (*in vacuo*, low temperature) and the resulting solids (7.0 g.) continuously extracted

(27) K. Auwers and J. A. Gardne, *Ber.*, **23**, 3622 (1890), give m.p. 187°.

with chloroform for 4 days. An infrared spectrum of the non-dissolved solid (5.6 g., 80%) indicated $\text{ABAH}_2^{++}2\text{Cl}^-$ and III. Ammonium chloride is also found in the chloroform-insoluble fraction. A slightly soluble oil (1.27 g., 17%) which separates from the chloroform solution slowly deposited crystals of III upon standing. The ultraviolet spectrum of this oil in water showed the presence also of the intermediate absorbing at 292.5 μ . Evaporation of the chloroform solution yielded 0.015 g. of a white solid whose infrared spectrum and m.p. are identical to tetramethyl-5-imino-2-pyrrolidone (IV) which was obtained in greater amounts from the photochemical degradation of $\text{ABAH}_2^{++}2\text{Cl}^-$ (see below).

Photochemical decomposition of $\text{ABAH}_2^{++}2\text{Cl}^-$ was carried out by storing in the sunlight of the laboratory a solution of $\text{ABAH}_2^{++}2\text{Cl}^-$ (270 g., 0.995 mole) in 2 l. of deoxygenated, demineralized water contained in a polyethylene bottle. After nearly 6 months there had precipitated approximately 20 g. (13% yield) of a white crystalline material, m.p. 285–288° dec., with NH band in the infrared at 3.08 μ and bands at 5.90(s) and 6.1(m) μ .

Hydrolysis of this compound under neutral (refluxing water, 24 hr.) or basic conditions (overnight, room temperature) produced tetramethylsuccinimide.

This compound is assigned the structure tetramethyl-5-imino-2-pyrrolidone (IV).

Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{N}_2\text{O}$: C, 62.3; H, 9.1; N, 18.2. Found: C, 62.3; H, 9.2; N, 18.1.

Tetramethylsuccinimidine nitrate was obtained by a procedure similar to that of Hammond and Neuman^{7a}: $\text{ABAH}_2^{++}2\text{NO}_3^-$ (0.3 g., 9.26×10^{-4} mole, obtained by addition of aqueous AgNO_3 to a solution of $\text{ABAH}_2^{++}2\text{Cl}^-$) was mixed with 2 ml. of anhydrous dimethyl sulfoxide and heated to 95°. Dissolution of material and loss of nitrogen occurred. After approximately 20 minutes, the solution was cooled and mixed with approximately 6 ml. of benzene. Just sufficient ethanol was added to give a homogeneous solution. After standing overnight, the white precipitate was filtered off, washed with ether and dried to yield 0.006 g. of tetramethylsuccinimidine nitrate (3% yield) whose infrared spectrum was identical to that of the sample supplied by Hammond and Neuman.^{7b} In dimethyl sulfoxide the sample showed λ_{max} 302.5 μ , ϵ 258.

To a sample of tetramethylsuccinimidine nitrate^{7b} (0.0040 g., 1.85×10^{-5} mole) in 5 cc. of ethanol was added 3 drops of 70% nitric acid. After 30 minutes the solvent was evaporated and the solids dried overnight to yield 0.0037 g. (92.5%) of material with an infrared spectrum essentially identical to starting imidine (N–H band at ~ 3.0 (s) μ , other bands at ~ 5.95 (w) and ~ 6.1 (m) μ) with the exception of an additional weak band at ~ 9.2 μ .

A similar sample left overnight in the acid solution yielded a material in which the 5.95 and 6.1 μ peaks had reversed in intensity.

Acknowledgments.—The author wishes to thank Drs. J. L. Hecht, J. J. Sparapany, D. F. Barringer Jr., and G. S. Hammond for suggestions and helpful discussions concerning this work.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

Changes in Reaction Order Due to Ion Association in the Reaction of Benzyl dimethylanilinium Ion and Thiocyanate Ion

By SIDNEY D. ROSS, MANUEL FINKELSTEIN AND RAYMOND C. PETERSEN

RECEIVED MAY 29, 1961

The rates of reaction of benzyl dimethylanilinium ion and thiocyanate ion to form benzyl thiocyanate and dimethylaniline have been studied in four solvents, *N*-methylpropionamide, benzyl alcohol, *s*-tetrachloroethane and chloroform. There are significant changes in reaction order in this series of solvents. These variations can be explained by considering the appropriate ion association equilibria and the specific rates for the reactions of ions and ion pairs.

In a previous report from this Laboratory,¹ it was shown that the rate of reaction of benzyl di-

(1) S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Am. Chem. Soc.*, **82**, 5335 (1960).

methylanilinium ion with ethoxide ion in ethanol varies with both changing initial concentrations and added neutral salts in a manner which is not satisfactorily accommodated by the Brønsted