for 2-amino-5-nitropyridine. 3,5-Dinitropyridine proved to be the most stable of the isomeric dinitropyridines. The calculated decomposition parameters suggested that 2,4,6-trinitropyridine is thermally stable. The calculated decompositions rates were about 1 order higher for the nitropyridines than for the nitrobenzenes, while the activation energies were on the average 12 kJ/mole lower.

The experimental data agreed with the results of theoretical calculations in showing that the presence of electron-acceptor substituents in the molecule reduces, and the presence of electron-donor substituents increases, the activation energy for thermal breakdown of the nitro compounds. This conclusion applies generally to the benzene and pyridine compounds covered by this work.

CONCLUSIONS

1. A study of the kinetics of gas-phase nitropyridine breakdown has led to the development of equations relating the kinetic decomposition parameters and the energy parameters of the molecule.

2. 2-Nitro-, 2-amino-5-nitro-, 4-nitro-, and 3,5-dinitropyridines decompose through $C-NO_2$ bond rupture. The energy required for bond rupture has been determined.

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KINETICS AND MECHANISM OF THE CYCLIZATION OF AMMONIUM SALTS CONTAINING PROPARGYL AND γ-PHENYLPROPARGYL GROUPS IN AQUEOUS POTASSIUM HYDROXIDE SOLUTION

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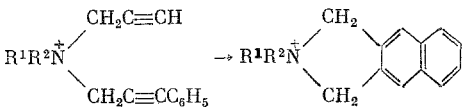
This is a continuation of work on the kinetics and mechanism of cyclization of ammonium salts containing propargyl and γ-phenylpropargyl groups in aqueous KOH solution [1, 2].

In the presence of catalytic amounts of alkali, dialkylpropargyl(γ-argylpropargyl)ammonium salts cyclize in aqueous solution to 5,6-benzoisoindolinium salts [3]



Intramolecular cyclization involving propargyl and 3-phenylpropargyl groups was first detected in the interaction of dimethylpropargyl(γ-phenylpropargyl)ammonium bromide with sodium ethoxide in ethanol [4]. The kinetics of cyclization of a series of salts with similar structures in dilute aqueous KOH solution have been examined [5], but the results precluded any definitive conclusions regarding the role of hydroxide in the reaction and its mechanism.

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TABLE 1

Salt	KOH, wt.%	$k_{ef} \cdot 10^2$, min^{-1}	Salt	KOH, wt.%	$k_{ef} \cdot 10^2$, min^{-1}	Salt	KOH, wt.%	$k_{ef} \cdot 10^2$, min^{-1}
(I)	5,19	0,5	(III)	5,4	1,79	(V)	1,4	0,062 *
	9,48	1,22		6,5	2,9		3,1	0,11 *
	9,83	1,23		7,5	3,1		6,3	0,34 *
	12,28	1,63		10,4	4,49		6,55	0,36
	14,96	2,5		13,45	7,55		8,35	0,385 *
	16,8	3,4		15,25	11,2		10,05	0,49 *
	19,75	4,8		17,35	13		10,1	0,53
	19,75	4,6 *		19,4	18		12,15	0,67 *
	24,4	8,7		20,3	21,4		15,2	1
	29,6	14,5		23,4	33,75		17,1	1,17
	31,85	16,4		25	38 *		19,9	1,65
	35,4	22,8		25,2	38,3		22,1	2,11
	38,85	25,8		27,75	56,5		22,2	2 *
	40,2	27,7		29,95	67,25		25,25	2,88
	41,45	28,9		30,8	69		27,45	3,12
							27,95	3,22 *
							31,2	4,28
							32,3	4,37
(II)	5,19	1,9	(IV)	1,95	3,9	(VI)	7,45	0,108
	6,35	2,6		2,5	5,1		7,65	0,096
	9,4	3,76		4	7,6		9,8	0,137
	11,35	5,82		5,4	10,5		12,35	0,19
	14	8,78		5,4	10,9		14,75	0,277
	17,1	11		7,5	15,2		17,05	0,39
	20,05	16,5		7,6	15,8		19,8	0,55
	22,05	21,3		8,65	16,9		23,45	0,843
	25,43	32		8,65	16,8 *		25,7	1,17
	26,8	44,6		10,3	20,3		26,95	1,3
				10,45	23		29,8	1,66
				12	26,6		32,25	2,09
				14	36,8		35,35	2,65
				14,6	36,6		36,55	2,88
				14,75	40		38,4	3,16
				16,95	48,9			
				17,2	51,3			
				17,4	51			
				18,95	58,4			
				19,9	67,1			
				20,6	70,1			
				22,55	86			

*We found k_{ef} from the change in optical density at the maximum of the absorption band of the reaction product. The other values of k_{ef} were found from the change in D at the maximum of the absorption band of the starting salt.

We have attempted to clarify the mechanism of the cyclization of salts of this series by examining the kinetics of cyclization involving propargyl and γ-phenylpropargyl groups in aqueous solution at 25°C over a wide range of KOH concentrations as exemplified by salts with various substituents on the N atom and in the benzene ring of the γ-phenylpropargyl group.

EXPERIMENTAL

We examined the kinetics of cyclization of the following bromide salts: methylpropargyl(γ-phenylpropargyl)ammonium (I) from 5.2% to 41.4% KOH; propargyl(γ-phenylpropargyl)piperidinium (II) from 5.2 to 26.8% KOH; propargyl(γ-phenylpropargyl)pyrrolidinium (III) from 5.4 to 30.8% KOH; propargyl(γ-phenylpropargyl)-morpholinium (IV) from 2 to 22.6% KOH; dimethylpropargyl(m-chlorophenylpropargyl)ammonium (V) from 1.4 to 32.3% KOH; and dimethylpropargyl(m-tolypropargyl)ammonium (VI) from 7.4 to 38.4% KOH.

We prepared salts (I)-(VI) and their cyclization products by the published procedure [6-8]. The KOH was chemically pure grade. Aqueous KOH solutions were prepared following [9]. We followed the kinetics spectrophotometrically at 240-245 and 275 nm with an SF-4A instrument. The kinetic curves could be described by the equation for first-order irreversible reactions. The apparent rate constant k_{ef} with fixed KOH concentration and temperature remained constant up to complete conversion of the starting salts to the cyclization products. The initial reagent concentrations were $(3-9) \cdot 10^{-5}$ mole/liter and KOH was always present in a large excess.

Cyclization of salts (V) and (VI) gave two isomers, (a) and (b)

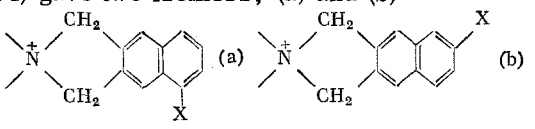


TABLE 2

KOH, wt.%	B_0	a_{H_2O}	$C^{free}_{H_2O}$	KOH, wt.%	B_0	a_{H_2O}	$C^{free}_{H_2O}$
2	−0,51	0,99	0,975	26	1,19	0,725	0,66
6	−0,055	0,975	0,925	30	1,415	0,65	0,61
10	0,245	0,94	0,875	34	1,665	0,575	0,55
14	0,495	0,895	0,825	38	1,94	0,485	0,49
18	0,725	0,845	0,765	42	2,215	0,37	0,425
22	0,95	0,79	0,715				

Note. Since $C^{free}_{H_2O}$ are quoted in relative units, k_{true} has the dimensions of min^{-1}.

TABLE 3

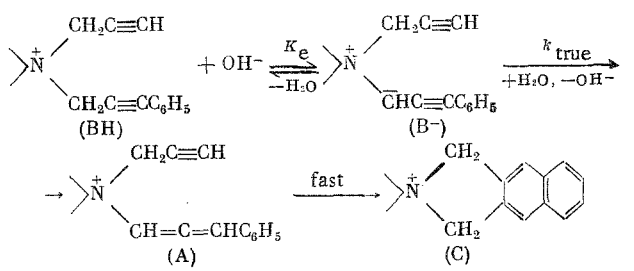
Salt	K_e	k_{true}, min^{-1}	$\left(\frac{k_{true}}{K_e}\right)\cdot 10^2$
(I)	96	0,78	0,8
(II)	>217	>5,8	2,7
(III)	>256	>7,7	3,0
(IV)	27,5	3,8	13,5
(V)	40,5	1,3	3,2
(VI)	106	1,0	0,9
(VII)	115	1,0	0,85

These isomers can be separated by recrystallization [8]; their UV spectra in water and aqueous KOH solutions are identical.

The rate data for salts (I)-(VI) are summarized in Table 1. Table 2 shows the values of the basicity of the medium b_0, the thermodynamic activity of water a_{H_2O}, and the concentration of free water $C^{free}_{H_2O}$ used in the calculations. For aqueous KOH solutions $b_0 = a_{\pm}$; we took the values of $a_{\pm}$, a_{H_2O}, and $C^{free}_{H_2O}$ from [10-12], respectively.

DISCUSSION

We have examined previously [1, 2] the kinetics of cyclization at 25°C of dimethylpropargyl(γ-phenylpropargyl)ammonium bromide (VII) from 5.4 to 44.7% KOH and of salt (IV), though the range of KOH concentrations was narrower than in the present work. Analysis of the rate data suggested the following reaction mechanism [1, 2]. In hydroxide solution the reactive form of the salt is formed in the fast and equilibrium stages of ionization. As a result of ionization carbanion (B^-) is formed and a water molecule is eliminated. The ionization center is the α-hydrogen of the γ-phenylpropargyl group. The concentration ratio of the ionized and un-ionized forms is described by the function b_0/a_{H_2O}. In the limiting stage interaction of carbanion (B^-) with a free water molecule forms a compound with the allene group (A). In the subsequent fast stage the end product of cyclization (C) is formed. Those H_2O molecules that are not strongly hydrogen bonded to OH^- ions are considered free



$$K_e = \frac{C_{BH} b_0}{C_{B^-} a_{H_2O}}.$$

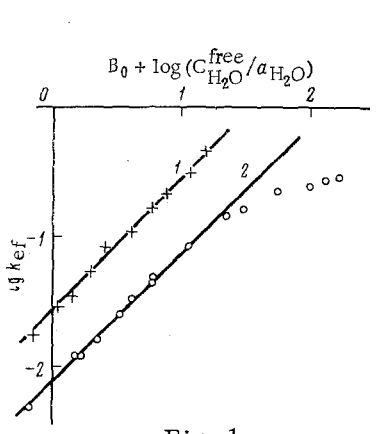


Fig. 1

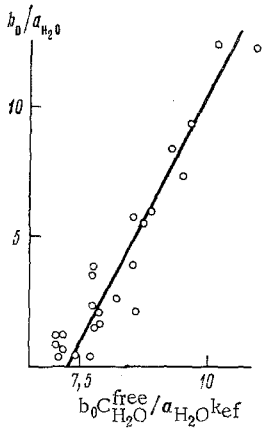


Fig. 2

Fig. 1. Plot of $\log k_{ef}$ against $B_0 + \log(C^{free}_{H_2O}/a_{H_2O})$ for the cyclization of 1) (II) and 2) (I) in aqueous KOH solutions at 25°C.

Fig. 2. Plot of b_0/a_{H_2O} against $b_0C^{free}_{H_2O}/k_{ef}a_{H_2O}$ for the cyclization of (IV) in aqueous KOH solutions at 25°C.

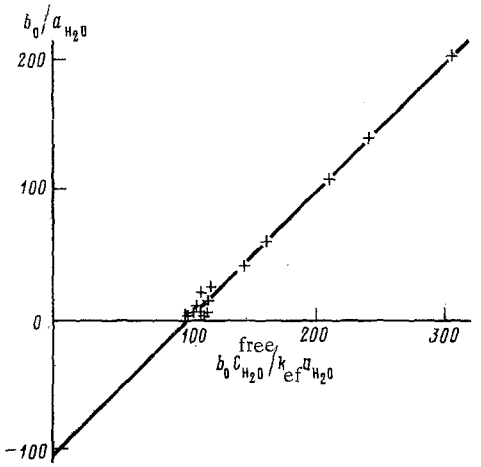


Fig. 3. Plot of b_0/a_{H_2O} against $b_0C^{free}_{H_2O}/k_{ef}a_{H_2O}$ for the cyclization of (VI) in aqueous KOH solutions at 25°C.

The starting salts also contain labile acetylenic α-hydrogens of the propargyl group, which in aqueous alkali solutions can be exchanged with the medium. However, the $R^1R^2R^3\overset{+}{N}\bar{C}HC{=}CH$ and $R^1R^2R^3\overset{+}{N}CH_2C{=}C^-$ anions are not reactive in cyclization; these species are not formed in substantial concentrations under the conditions of the kinetic runs.

We did not isolate compound (A) with the allene group but inferred its formation on the basis of the stoichiometry of the limiting stage. However, another interpretation of the mechanism is possible: in the limiting stage in attack, ring formation via the allene-like structure takes place during attack by the water molecule on the (B^-) ion. In this case (A) is not the chemical intermediate in the cyclization reaction. We chose between these two possibilities for the mechanism of the limiting stage on the basis of the effect of the meta substituents in the phenyl ring of the γ-phenylpropargyl group on the kinetics of cyclization.

According to this scheme, the expression for the reaction rate W is

$$W = k_{true}\frac{a^{\neq}}{f^{\neq}} = k_{true}C_{B^-}C^{free}_{H_2O}\frac{f_{B^-}f^{free}_{H_2O}}{f^{\neq}} \qquad (1)$$

where k_{true} is the true rate constant for disappearance of the (B^-) ions in the limiting stage; f is the activity coefficient; and $a^{\neq}$ is the activity of the activated complex.

If we write C_{B^-} in terms of b_0 and a_{H_2O} and assume that the factor of the activity coefficients does not depend on the catalyst concentration in the solution, then

$$k_{ef} = \frac{W}{C_0} = \frac{k_{true}}{K_e} \frac{b_0 C_{H_2O}^{free}/a_{H_2O}}{1 + b_0/a_{H_2O}K_e} \quad (2)$$

where C_0 is the overall concentration of the unreacted salt ($C_0 = C_{BH} + C_{B^-}$). Equation (2) applies to the general case where there are high concentrations of the reactive carbanion in the solution ($C_{BH} \sim C_{B^-}$).

The validity of this mechanism of the cyclization of the salts with this structure is illustrated below by the agreement of our rate data with Eq. (2). The functional dependences of k_{ef} on the thermodynamic properties of the medium are shown as graphs from Eqs. (3) and (4). We derived (3) by transforming Eq. (2) to cartesian coordinates. Equation (4) is a special case of (2) given a low degree of reactant ionization ($C_{B^-} \ll C_{BH}$, $C_{BH} = C_0$)

$$b_0/a_{H_2O} = k_{true} \frac{b_0 C_{H_2O}^{free}}{a_{H_2O} k_{ef}} - K_e \quad (3)$$

$$\lg k_{ef} = \lg (k_{true}/K) + B_0 + \lg (C_{H_2O}^{free}/a_{H_2O}) \quad (4)$$
$$B_0 = \lg b_0$$

When (4) is valid, the plot of $\log k_{ef} - B_0 + \log (C_{H_2O}^{free}/a_{H_2O})$ should be linear with slope one. The deviation from the straight line in the coordinates of (4) implies that the reactant is strongly ionized in the solution. Analysis of the rate data by Eq. (3) provides k_{true} and K_e separately, while Eq. (4) gives the ratio of the constants k_{true}/K_e.

Equations (4) are valid for these salts over a wide range of KOH concentrations (Fig. 1). This we believe to support the suggestion that the activity coefficient factor remains constant when the KOH concentration changes. For salts (I), (IV)-(VI) we also got values of k_{ef} for KOH solutions containing a relatively high concentration of the reactive form B^-. For these we found k_{true} and K_e graphically from Eq. (3) (Figs. 2 and 3). Table 3 shows our values of the constants k_{true} and K_e and their ratio salts for (I)-(VI) and also for salt (VII) from our earlier figures [1].

The ratio of the constants k_{true}/K_e can be used to assess the overall effect of the substituents on the reactivity of the salts in cyclization. Our figures give the order of reactivity of the salts as (IV) > (III) > (II) > (VII) > (I). This is valid since these salts have a common mechanism. We can also compare the effect of the substituent on k_{true} and K_e separately. We can estimate only the lower limits to the constants k_{true} and K_e for salts (II) and (III). When calculating these constants, we assumed that the ratio $C_{B^-}/C_0 < 10\%$ in the runs with the highest KOH concentration. We carried out this run at 26.8% KOH and $b_0/a_{H_2O} = 24.1$ for salt (II) and at 27.7% KOH and $b_0/a_{H_2O} = 28.4$ for salt (III).

For salt (II), $K_e > (0.9/0.1) b_0/a_{H_2O} = 217$ and $k_{true} > 5.8$ min^{-1}.

For salt (III), $K_e > 256$ and $k_{true} > 7.7$ min^{-1}.

Table 3 suggests several conclusions regarding the effect of the nitrogen substituents on the limiting and equilibrium stages. Our comparison was based on salt (VII). Replacement of one CH_3 group by propargyl slightly promotes the ionization of the reactant. Conversely, replacement of two CH_3 groups by piperidinium or pyrrolidinium markedly inhibits the ionization process. Allene formation is promoted in the pyrrolidinium and piperidinium salts relative to salt (VII) but inhibited by replacement of the CH_3 group by propargyl. The substituent effect is in qualitative agreement with the change in the Taft inductive constants for these groups [13]. Among these salts we note the morpholinium salt (IV), in which ionization is about four times easier and allene formation 3.8 times easier.

Comparison of k_{true} and K_e of salts (V)-(VII) can be used to choose between the two possibilities for the mechanism of the limiting stage. Chlorine and the CH_3 group, being ortho-para directing, affect the ring formation stage in the following way. The CH_3 group in the meta position of the benzene ring promotes ring formation but does not affect allene formation. Chlorine has the opposite effect on these two processes: the

Cl atom in the m position promotes allene formation but inhibits ring formation. Table 3 shows that k_{true} is higher in (V) than in salt (VII), whereas we get identical values of k_{true} for salts (VI) and (VII). This suggests that the limiting stage is formation of the allene group and that ring formation takes place in the fast stage. Table 3 also shows that because of its negative inductive effect the Cl atom promotes ionization of salt (V) by a factor of ~2.8.

CONCLUSIONS

1. We have used a spectrophotometric method to examine the kinetics of the cyclization of methyldipropargyl(γ-phenylpropargyl)ammonium, propargyl(γ-phenylpropargyl)piperidinium, propargyl(γ-phenylpropargyl)pyrrolidinium, propargyl(γ-phenylpropargyl)morpholinium, dimethylpropargyl(m-chlorophenylpropargyl)ammonium, and dimethylpropargyl(m-tolylpropargyl)ammonium bromides in aqueous solution over a wide range of KOH concentrations at 25°C.

2. The catalytic effect of aqueous alkali solution is apparent in the equilibrium ionization of the salts involving cleavage of the α-hydrogen of the γ-phenylpropargyl group. The rate of the limiting stage is controlled by the concentrations of the carbanion and free water molecules. We have measured the rate constants of the limiting stage and the equilibrium constants of the ionization stage.

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