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Kinetics of Formation and Reactions of Quaternary Ethylenimonium Compounds

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The rates of formation of ethylenimonium compounds from $(CH_3)_2NCH_2CHBrCH_3$ and from $RR'NCH_2CH_2X$, where $R = R' = H$, $R = R' = CH_3$, $R = R' = CH_3CH_2$, $R = R' = (CH_3)_2CH$, or $R = CH_3$, $R' = (CH_3)_2CH$ and $X = Br$ or Cl, have been measured at 25° and $\mu = 0.07$ in aqueous solution. The rate constants increase strongly with the size of R and R′ from 5.6×10^{-4} sec^{-1} for $R = R' = H$, $X = Br$ to about 25 sec^{-1} for $R = R' = (CH_3)_2CH$, $X = Br$. To explain these results it is proposed that the rate depends to some extent on the electron density at the nitrogen atom but mainly on the amount of energy necessary to change the bond angles at the nitrogen atom. These angles are different in the amine and in the ethylenimonium ion. The influence of R and R′ on the rates of the opening of the ethylenimonium rings by thiosulphate ions was found to be small. The smallest value at 25° and $\mu = 0.07$ was 2.38×10^{-2} for $R = R' = H$ and the greatest 1.89×10^{-1} l $mole^{-1}$ sec^{-1} for $R = R' = (CH_3)_2CH$. The rate measurements were made with a recording pH-stat.

One conceivable mechanism for the decomposition of 2-dialkylaminoethyl acetates in alkaline water solution is the formation of N,N-dialkylethylenimonium acetates [1]. For that reason it was necessary to study the influence of the N-alkyl groups on the rates of reactions at which N,N-dialkylethylenimonium compounds are known to be formed. As starting materials for such studies 2-dialkylaminoethyl halides are useful.

The rates of cyclization of primary ω-haloalkylamines as 2-bromoethylamine were measured by Freundlich and co-workers [2] in the period 1911–1933. A theoretical treatment of their work has been done by Salomon [3–5]. The decomposition of "nitrogen mustards", *i.e.* tertiary amines containing two 2-chloroethyl groups, has been thoroughly investigated by several authors [6–12]. Simonetta *et al.*[13] describe the kinetics of the cyclization of 2-dimethylaminoethyl chloride.

It is well known that ethylenimines and -imonium compounds easily react with nucleophilic reagents such as water, amines, hydroxyl and thiosulphate ions. Extensive studies in this field have been carried out by Clapp and his collaborators [14] and also by other investigators [6–9, 11, 12].

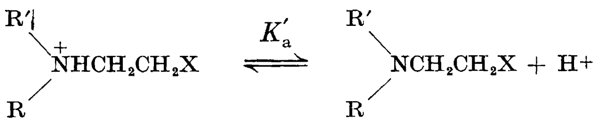
In this paper the rates of the cyclization of 2-aminoethyl bromide and of six 2-dialkylaminoethyl halides in aqueous solution are reported. Furthermore, as the rates were found to be unexpectedly strongly influenced by the N-alkyl groups, it was of interest to measure the rates of the reactions between the ethylenimonium compounds formed and thiosulphate ions. Special methods for the rate measurements with the use of a pH-stat have been worked out.

THEORY OF THE RATE MEASUREMENTS

For the determinations of the reaction rates indirect methods were used. They were based on the fact that hydrogen ions were formed during the formation of ethylenimonium ions and consumed in the reaction between these and thiosulphate ions. The amounts of alkali or acid necessary to keep the pH of the reaction mixture constant by automatic titrations were recorded[15]. The records were used for calculations of the velocity constants.

Cyclization of 2-dialkylaminoethyl halides

The method of the determination of the rate of the formation of ethylenimonium ions is similar to the method used for the determination of the rates of alkaline hydrolysis of aminoalkyl esters[16].

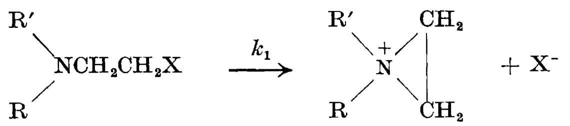

(1)

I II

$$\frac{c_{II}a_{H^+}}{c_I} = K_a' \tag{2}$$

c = concentration, a = activity

In water solution there is an equilibrium (1) between the acid form, I, and the basic form, II, of the aminoethyl halide. Only II is able to form an ethylenimonium ion. This reaction (3) is first order and has the rate constant k_1.


(3)

When the reaction (3) is running the equilibrium (1) is disturbed. But it is immediately corrected by the dissociation of I which results in the formation of hydrogen ions. These must be titrated with alkali to keep the pH constant. In order to obtain a practically measurable alkali consumption the amount of I must not be too small, that is the pH-value must be smaller or only slightly greater than the pK_a'-value. It can be shown (*cf.* Ref.[1], eqn. (11)) that the

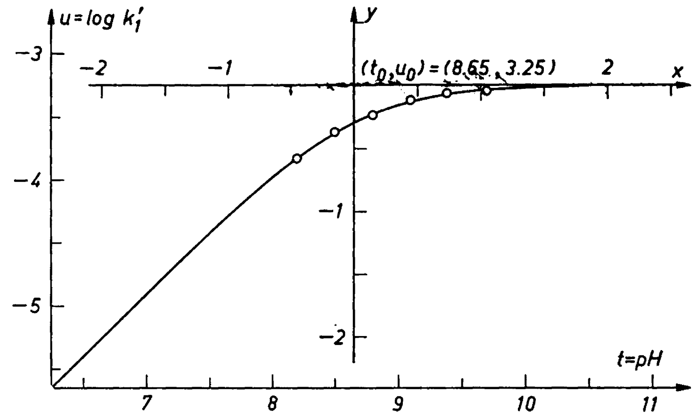


Fig. 1. Plot of the rate of cyclization of 2-bromoethylamine as function of pH, fitting the standard curve given by eqn. (5).

rate of alkali consumption, k_1', calculated from titration records, is first order and related to k_1 according to eqn. (4)

$$\log k_1' - \log k_1 = \log[1/(1 + 10^{-(\mathrm{pH}-\mathrm{p}K'_a)})] = -\log(1 + a_{\mathrm{H}^+}/K_a') \qquad (4)$$

Eqn. (4) shows that knowledge of the value of K_a' is necessary for the calculation of k_1 from k_1'. As K_a' was unknown for all the amines the following method was used.

Values of k_1' were measured at a number of pH-values. When $u = \log k_1'$ was plotted against $t = \mathrm{pH}$ (Fig. 1) two types of diagrams were obtained: (A) containing a curved line as in Fig. 1, or (B) containing a straight line with the slope $+45°$.

(A) Curved lines are obtained if in the last term of (4) neither 1 nor a_{H^+}/K_a' may be neglected, *i.e.* when the measurements are carried out in a pH-region around $\mathrm{p}K_a'$. The experimental curve drawn on a transparent paper is moved to fit, with parallel axis (Fig. 1), as well as possible a standard curve

$$y = \log[1/(1 + 10^{-x})] \qquad (5)$$

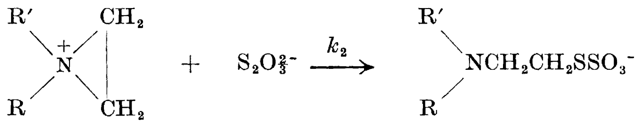
The origin ($x = 0$, $y = 0$) of the coordinate system of the standard curve is marked on the experimental diagram and its coordinates (t_o, u_o) are read off (Fig. 1). It is easy to show that $t_o = \mathrm{p}K_a'$ und $u_o = \log k_1$.

(B) A straight line with a slope of $+45°$ is the result of the plot if the value of k_1 is so great that it is necessary to determine k_1' at pH-values at which the concentration of free amine is only a very small fraction of the total amine concentration, *i.e.* when $a_{\mathrm{H}^+}/K_a' \gg 1$ or $\mathrm{pH} \ll \mathrm{p}K_a'$. In this case eqn. (4) may be simplified to

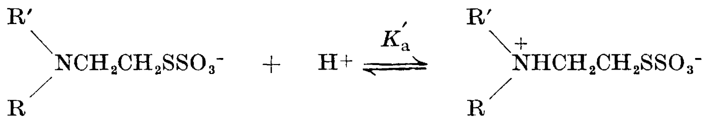
$$\log k_1' - \log k_1 = \mathrm{pH} - \mathrm{p}K_a' \qquad (6)$$

which is the equation of a straight line with a slope of $+45°$ (the left part of the curve in Fig. 1). No determination of K_a' or k_1 is possible by any method. But if K_a' can be estimated, eqn. (6) can be used for an estimation of k_1.

Reactions between N,N-dialkylethylenimonium and thiosulphate ions



(7)



(8)

The opening of the ethylenimonium ring is in principle the reverse of the ring formation. This fact is recognized if the formulas (7) and (8) are compared with (3) and (1). That means that if the pH-value of the reaction mixture is smaller than or near the value of pK_a' of the amine formed, the ring opening is accompanied by a measurable consumption of hydrogen ions. The rate of this consumption, k_2', can be calculated from automatic, recorded titrations at constant pH. The rate of reaction (7) is in the pH-range around 7 independent of pH as both of the reactants are only involved in dissociation equilibria to a negligible extent. It is then easy to calculate k_2 from k_2' and the concentration of thiosulphate ions. This concentration can be kept constant by automatic addition of sodium thiosulphate.

$$k_2 = k_2'/c_{S_2O_3^{2-}} \qquad (9)$$

EXPERIMENTAL

Materials

N,N-Dialkyl-2-bromoethylammonium bromides. The compounds were obtained from the corresponding aminoethanols and 50 % excess of hydrobromic acid. The reaction mixture was heated in an oilbath, and water was slowly distilled off through a 25 cm Widmer column. When the boiling point of the distillate had reached 125°, the residue was evaporated under reduced pressure to dryness. The crude products were recrystallized from acetone or absolute ethanol until the analyses in Table 1 were obtained.

N,N-Diethyl-2-chloroethylammonium chloride was obtained from 2-diethylaminoethanol and thionyl chloride [18] and recrystallized from absolute ethanol. For analyses see Table 1.

Kinetic measurements

The kinetic measurements were carried out as titrations at constant pH using an automatic recording titrator [15]. This gave records of the amount of titrant used as a function of time. From the records pseudo-first-order rate constants were calculated.

Table 1. Analyses and melting points of some 2-haloethylammonium halides. The melting points have been determined on a Kofler heating table.

Formula	Mol. wt.	M.p.		Analyses			
				C		H	
		Found	Lit.	Found	Calc.	Found	Calc.
$[H_3\overset{+}{N}CH_2CH_2Br]Br^-$	204.9	174°	172.5–173.5°[19]	11.7	11.7	3.6	3.62
$[(CH_3)_2\overset{+}{N}HCH_2CH_2Br]Br^-$	233.0	194°	188.5–188.9°[20]	20.6	20.6	4.6	4.76
$[(CH_3CH_2)_2\overset{+}{N}HCH_2CH_2Br]Br^-$	261.0	217°	208.1–208.4°[20]	27.8	27.6	5.7	5.80
$[((CH_3)_2CH)_2\overset{+}{N}HCH_2CH_2Br]Br^-$	289.1	141°	–	33.2	33.2	6.5	6.63
$[(CH_3)_2CH\overset{+}{N}H(CH_3)CH_2CH_2Br]Br^-$	261.0	122°	–	27.3	27.6	5.6	5.79
$[(CH_3)_2\overset{+}{N}HCH_2CHBrCH_3]Br^-$	247.0	199°	–	24.4	24.3	5.1	5.31
$[(CH_3CH_2)_2\overset{+}{N}HCH_2CH_2Cl]Cl^-$	172.1	216°	210 –211°[10]	41.7	41.9	8.8	8.77

The reactions took place under nitrogen atmosphere in a thermostated glass vessel at 25.00 ± 0.05°. The electrodes used, a Radiometer glass electrode type G 202 A (for 2-bromoethylamine type G 202 B), and a Radiometer saturated calomel electrode typ K 401, were standardized against 0.05 M potassium hydrogen phthalate, pH 4.01. In order to reduce the pH-fluctuations, which were less than ± 0.01 pH-unit, the buffer capacity of the reaction mixture was increased to about 9×10^{-5} equiv.l.$^{-1}$ (pH-unit)$^{-1}$ by adding small amounts of acetic acid or potassium dihydrogen phosphate solutions in the pH-region 4.6–9.4. No influence on the rates by these additions could be observed.

Cyclization of 2-aminoethyl halides. In each experiment $(1.3-1.6) \times 10^{-5}$ mole of 2-haloethylammonium halide was dissolved in 30 ml of 0.07 M potassium perchlorate solution and 0.1–1 ml of 0.05 M acetic acid or 0.05 M potassium dihydrogen phosphate solution and titrated at desired pH with 0.020 M sodium hydroxide solution from a 0.5 ml syringe. More concentrated solutions than 0.07 M potassium perchlorate were found to disturb the constancy of the e.m.f. of the calomel electrode. Potassium perchlorate was chosen instead of potassium chloride to give a constant ionic strength of the solution because perchlorate ions are known to react slower than chloride ions with ethylenimonium ions [14]. Rate determinations were carried out at least at 4 pH-values for each compound. Table 2 contains the results.

Reactions with thiosulphate ions. $(1.2-1.3) \times 10^{-5}$ mole of 2-haloethylammonium halide was dissolved in enough water and 0.07 M potassium perchlorate solution so that the ionic strength, $\mu = \frac{1}{2} \Sigma c_i z_i^2$, of the reaction mixture later after addition of sodium thiosulphate solution became 0.07. The mixture was titrated with 0.1 M sodium hydroxide solution at a pH such that at least 99.8 % of the amine had formed ethylenimonium ions in about 20 min. An exception was the formation of ethylenimine from 2-bromoethylamine which required 3 h at pH 9.0. After addition of 0.10 ml of 0.05 M potassium dihydrogen phosphate solution and adjustment of the pH to about 6.8 (for ethylenimine [14], $pK_a' = 8.0$, to 5.2) 1.50 or 3.00 ml of 0.101 M sodium thiosulphate solution was added. The total volume was now 30 ml. The ring opening reaction was followed by titration with 0.5 ml of 0.020 M hydrochloric acid solution. In order to keep the thiosulphate ion concentration constant in the reaction mixture 0.020 M sodium thiosulphate solution was added at the same rate as the hydrochloric acid solution [17]. Table 3 contains the results.

Table 2. pK_a' of and rate constants of the cyclization of some 2-haloethylamines. Temperature 25°. μ = 0.07. Unit of k_1 and k_1', sec^{-1}.
$pK_a = pK_a' - 0.10$

Compound	pK_a'			pH at which $\log k_1' = -3.5$	$\log k_1$			Measurements in pH-range
	found	estimated	lit.		found	estimated $\pm$ 0.2	lit.	
$NH_2CH_2CH_2Br$	8.65 $\pm$ 0.02		8.49/24° [21]	8.80 $\pm$ 0.01	−3.25 $\pm$ 0.01		−3.22 [22]	8.20−9.70
$(CH_3)_2NCH_2CH_2Br$		8.0		6.51 $\pm$ 0.01		−2.0		6.10−7.15
$(CH_3CH_2)_2NCH_2CH_2Br$		8.7		5.60 $\pm$ 0.01		−0.4		5.20−6.25
$((CH_3)_2CH)_2NCH_2CH_2Br$		9.0		4.06 $\pm$ 0.01		+1.4		3.70−4.45
$(CH_3)_2CHN(CH_3)CH_2CH_2Br$		8.7		5.54 $\pm$ 0.01		−0.4		5.20−6.10
$(CH_3CH_2)_2NCH_2CH_2Cl$	8.80 $\pm$ 0.04		8.6 [10]	7.35 $\pm$ 0.01	−2.03 $\pm$ 0.05		−2.02 [10]	7.00−8.05
$(CH_3)_2NCH_2CHBrCH_3$		8.0		5.86 $\pm$ 0.01		−1.1		5.50−6.40
$(CH_3)_2NCH_2CH_2Cl$							−3.54 [13]	

Table 3. Rate of the reactions between ethylenimonium and $S_2O_3^{2-}$-ions. Temperature 25°. μ = 0.07.

Compound	$c_{S_2O_3^{2-}}$ mmole l^{-1}	$10^2 \times k_2$ l mole^{-1} sec^{-1}	
		found ± 3 %	lit.
$H_2\overset{+}{N}CH_2CH_2$	10.1	2.38	0.536 [14]
$(CH_3)_2\overset{+}{N}CH_2CH_2$	10.1	8.65	
$(CH_3CH_2)_2\overset{+}{N}CH_2CH_2$	10.1	5.66	
	5.05	5.74	
$((CH_3)_2CH)_2\overset{+}{N}CH_2CH_2$	5.05	18.9	
$(CH_3)_2CH\overset{+}{N}(CH_3)CH_2CH_2$	5.05	4.71	
$(CH_3)_2\overset{+}{N}CH_2CHCH_3$	10.1	3.00	

RESULTS

The rates of cyclization of 2-haloethylamines to ethylenimines (Table 2) were slow enough only in the case of 2-bromoethylamine and 2-diethylaminoethyl chloride to make it possible to determine the true rate constant, k_1, and the pK_a' of the amine. The errors of k_1 and pK_a' were estimated from the largest deviations that could be made without getting an unacceptable fit between the experimental and the standard curve. The literature values for 2-diethylaminoethyl chloride are extrapolated from values determined at 0° and 15°.

For the other compounds the plot of log k_1' against pH gave straight lines with the expected angle coefficient = 1, except for 2-diisopropylaminoethyl bromide. In this case the slope of the straight line was 1.16, *i.e.* a tenfold increase of the hydrogen ion concentration decreased the k_1'-value 14.5 times. No explanation of this phenomenon has been found yet, and it was not taken into consideration at the estimation of k_1.

The pK_a'-values of those compounds for which no pK_a' could be determined were calculated according to Hall [23]. From the equation $pK_a = 13.23 - 3.14\ \Sigma\sigma^*$, the observed value $pK_a = 8.55$ for 2-bromoethylamine and $\sigma^* = 0.49$ for NH, the value $\sigma^* = 0.51$ was calculated for NCH_2CH_2Br. This value, combined with $\sigma^* = 0.00$ for NCH_3, -0.10 for NCH_2CH_3, -0.19 for $NCH(CH_3)_2$ and -0.30 for $N(CH(CH_3)_2)_2$ [1] and the equation $pK_a = 9.61 - 3.30\ \Sigma\sigma^*$, then gives the estimated pK_a'-values of Table 2. From these pK_a'-values and the pH-values at which log $k_1' = -3.5$ the estimated log k_1-values were obtained when eqn. (6) was used.

The k_1-values (Table 2) of the cyclization reaction (1) are in good agreement with those found in the literature. The influence of the ionic strength seems to be small as Freundlich's and Kroepelin's k_1-value of 2-bromoethylamine [22] has been measured in a solution with $\mu = 0.15$ and the k_1-value of 2-diethylaminoethyl chloride obtained by Cohen *et al.*[10] refers to a solution with $\mu = 0.0025$. Nor is a great influence expected as the reacting molecule is uncharged and the reaction is intramolecular.

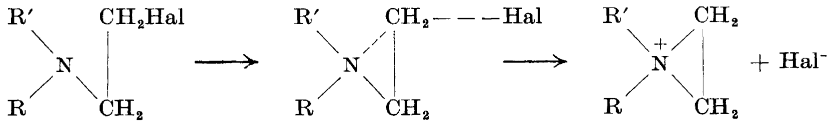
The deviations of the pK_a'-values now obtained from those found in other papers may be due to two facts. Firstly, the later values were determined in solutions with $\mu = 0.0025-0.01$ which gives smaller pK_a'-values than if $\mu = 0.07$. Secondly, these values were determined from pH-measurements of solutions of the haloethylammonium salts partly titrated with sodium hydroxide solution, which because of the cyclization must give somewhat unreliable values.

When the values of the rates of the reactions between the ethylenimonium and the thiosulphate ions (log k_2 in Table 3) were calculated, reactions of the ethylenimonium ions with other species, *i.e.* perchlorate ions and water, were not considered. The rates of these side reactions are unknown but must be so small that they may be neglected in comparison with the first mentioned reaction [14]. A proof for this assumption is an experiment in which 1.00 equivalent of diisopropylaminoethyl bromide hydrobromide was found to liberate 1.00 equivalent of hydrogen ions during the cyclization and after one hour at pH 6.0 and 25° consume 1.00 equivalent of hydrogen ions during the reaction with thiosulphate ions. No hydrolysis of the formed thiosulphate esters could be detected even if pH was as high as 10.

The large deviation of the literature value of log k_2 of the N-unsubstituted ethylenimonium ion refers to measurements in a solution with $\mu = 1.0$. The difference may to a great extent be due to difference of the ionic strengths as the rate of reactions between ions of opposite charges normally increases when the ionic strength is decreased [24].

DISCUSSION

For a great number of bimolecular reactions of tertiary amines the general rule is that increased branching at the 1-carbon atom reduces the reaction rate [25]. However, in the cyclization of 2-haloethylamines the effect of such branching is opposite (Table 2).



The cyclization may be regarded as an intramolecular nucleophilic substitution reaction. The alkyl groups at the 1-carbon atoms of R and R′ may effect the reaction velocity in two ways, partly, by influencing the steric conditions

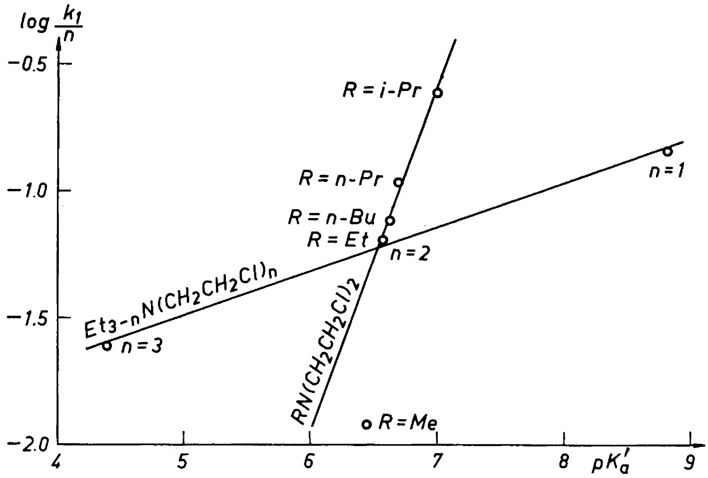


Fig. 2. Plot [10] of $\log(k_1/n)$ *versus* pK_a' for some 2-chloroethylamines, $R_{3-n}N(CH_2CH_2Cl)_n$, at 15°.

and, partly, by influencing the electron density at the nitrogen atom and by that its nucleophilic property.

Table 2 shows that each methyl group on the 1-carbon atoms increases the value of $\log k_1$ by 0.8—1.0 units and also increases pK_a' [23]. Similar values were obtained by Cohen *et al.*[10] in their studies of the formation of ethylenimonium compounds from N-alkyl-bis(2-chloroethyl)amines with the N-alkyl groups methyl, isopropyl, ethyl, propyl and butyl. They also found, that pK_a' and $\log k_1$ of the last three compounds were constant within $\pm$ 0.1 units, showing that the influence on $\log k_1$ and pK_a' of the alkyl groups at the 2-carbon atoms is much smaller than of such groups at the 1-carbon atoms.

The existence of a linear relationship between pK_a', which may be regarded as a measure of the electron density at the nitrogen atom, and $\log k_1$ was shown by Cohen *et al.*[10] If in their series the N-methyl compound was excepted, a plot of $\log k_1$ *versus* pK_a' (Fig. 2) gave a straight line with a slope of + 1.4 ($\log k_1$)-units/pK_a'-unit.

If we assume that there are no steric effects in the cyclization, the same slope will be obtained when for the three compounds

$$(CH_3CH_2)_{3-n}N(CH_2CH_2Cl)_n, \; n = 1, \; 2 \;, \text{or } 3,$$

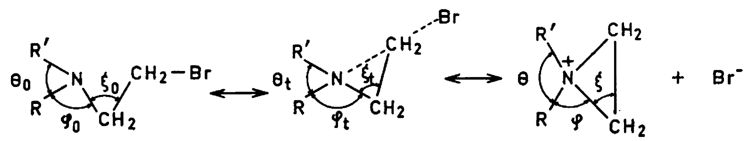
$\log(k_1/n)$ is plotted against pK_a'. The plot gives a straight line (Fig. 2) but the slope is much smaller, namely + 0.18 ($\log k_1$)-units/pK_a'-unit. The choice of $\log(k_1/n)$ as a coordinate is due to the fact that the probability for cyclization may roughly be considered to be proportional to the number of $ClCH_2CH_2$-groups.

On the other hand, assume that only the steric conditions affect the reaction rate. If this is correct $\log(k_1/n)$ will have the same value $\pm$ 0.1 unit for all the compounds $(CH_3CH_2)_{3-n}N(CH_2CH_2Cl)_n$ as the chlorine atoms are substituents on the 2-carbon atoms. But in fact $\log(k_1/n)$ decreases by about 0.4 units for each chlorine atom.

From what is said above the conclusion may be drawn that the rate of cyclization of tertiary 2-haloethylamines depends for a given halogen atom mainly on the number of alkyl groups on the 1-carbon atoms and to some extent on the electron density at the nitrogen atom.

The departing halide ion does not seem to have any influence on the relative rate of cyclization of two homologous 2-haloethylamines. A proof of this statement is that the difference between the log k_1 values for the dimethylamino- and the diethylaminoethylhalides is the same regardless of whether the halide is chloride or bromide.

The material now available is too small for an explanation of the reaction mechanism, but the following theory is proposed. In the N,N-dialkyl-ethylenimonium ion the angle ω between the ring bonds is about 60°. Thus the other bond angles, φ and Θ at the nitrogen atom must be somewhat greater than



at a tertiary or quaternary nitrogen atom of an acyclic compound. Accordingly, for the formation of the transition state a part of the activation energy must be used to change the bond angles Θ_o, φ_o, and ξ_o. If R and R' are bulky groups, it can be assumed that Θ_o and φ_o have values closer to Θ_t and φ_t than if R and R′ are small. This means that the formation of a transition state should be fascilitated and the reaction rate higher when R and R' are big, for the energy released during the completion of the ring closure should be rather independent of R and R′.

For similar reasons one may expect that the N,N-dialkylethylenimonium ring will be stabilized by bulky alkyl groups. In order to determine if this would hold true the rates of the reactions of these compounds with thiosulphate ions were measured (Table 3). But no simple relation was found between the size of the substituents at the nitrogen atom and the second order rate constants k_2. If the N-alkyl groups have only an inductive effect, k_2 for the di-isopropyl compound would have the smallest value, but it has the largest. There must accordingly be other effects, for instance steric ones, that are of greater importance for the reactions.

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