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MECHANISM OF AMINATION OF AZIRIDINES AND OXIRANES.

3. QUANTUM-CHEMICAL INVESTIGATION OF THE EFFECTS OF SPECIFIC SOLVATION

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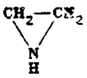
The characteristics of the associates formed by the aziridine and ethylene oxide molecules in protic solvents were studied by the nonempirical SCF MO-LCAO quantum-chemical method in the STO-3G basis set. It was shown that the main reacting particles in the acid-catalyzed ammonolysis reactions are ethylene oxide—ammonium cation and protonated aziridine—solvent complexes.

It is known that unactivated aziridine (I) and oxirane (II) have low reactivity in the nucleophilic addition of ammonia [3]. The reaction is accelerated appreciably with catalysis by acids and ammonium salts [4]. It is usually considered that under the conditions of acid catalysis the protonated forms of aziridine and ethylene oxide (III, IV) enter into reaction with the ammonia at the controlling stage [5].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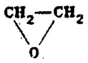
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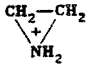
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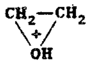
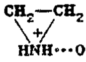

IV

However, the formation of a whole series of associates, including the molecules of the three-membered rings, the proton, and the solvent molecules, is possible in the aqueous ammonia solutions in which these processes are usually realized [6]. The question of the reactivity of the above-mentioned intermediate products remains open. In view of the great theoretical and practical significance of these processes and also of the complexity of the experimental investigation of their kinetics, in the present work we attempted to calculate the reactivity of the complexes of aziridine and ethylene oxide with the solvent under the conditions of acid catalysis.

We undertook nonempirical calculations using the minimal basis set of the STO-3G orbitals. The calculations in the minimal basis set make it possible to describe satisfactorily the stabilization arising through the hydrogen bond, although they appreciably overestimate its energy. The complexes which can be formed by aziridine and ethylene oxide with the proton and with one water or ammonia molecule were considered. By the calculations in the STO-3G basis set we discovered the stable complexes (V-VIII). (In the structural formulas of the complexes the proton attached both to the molecule of the three-membered ring and to the solvent molecule was considered to "belong" to the heteroatom from which it was separated by the shortest distance.)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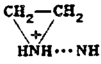
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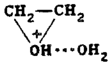
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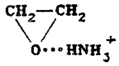
VIII

State Institute of Applied Chemistry, Leningrad. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1036-1041, August, 1986. Original article submitted June 4, 1985.

TABLE 1. The Energy Characteristics of the Complexes, Determined by the STO-3G Method

Compound	Total energy, au	Heat of complex formation, kJ/mole
V	−206,8474	−141,9
VI	−187,3484	−172,1
VII	−226,3466	−216,0
VIII	−206,8529	−146,1
XIV	−281,8503	−239,1*
XV	−242,8444	−278,9*

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*The heat of formation of the complex from the molecule of the three-membered ring and the two isolated solvent molecules.

TABLE 2. The Geometric Characteristics of the Three-Membered Rings (I-IV) and the Complexes (V-VIII, XIV, XV) According to Data from STO-3G Calculations*

Compound†	Structural parameters‡													
	a	*b*	*c*	*d*	*e*	*f*	*g*	α	β	γ	δ	ε	λ	μ	ν
I	1,084	1,491	1,482	1,042				150,0	56,3	156,4	57,8	110,3			
II	1,088	1,483	1,433					155,3	57,3	155,3	57,3				
III	1,091	1,493	1,509	1,037	1,037			159,4	58,1	159,4	58,1	123,6	123,6		
IV	1,095	1,490	1,492	0,999				160,2	57,6	163,7	58,7	117,8			
V	1,088	1,490	1,494	1,148	1,033	1,281	0,983	158,2	58,0	156,3	57,6	125,0	119,1	118,2	105,4
VI	1,087	1,491	1,489	1,210	1,033	1,297	1,032	157,7	57,8	155,3	57,5	127,0	117,6	112,3	
VII	1,091	1,486	1,455	1,152		1,174	0,983	157,7	57,7	161,1	58,2	123,0		115,7	106,7
VIII	1,090	1,486	1,446	1,245		1,183	1,034	156,9	57,6	159,8	57,9	127,7		111,4	
XIV	1,086	1,490	1,484	1,096	1,096	1,392	0,982	156,1	57,6	156,1	57,6	121,6	121,6	121,8	104,2
XV	1,086	1,490	1,480	1,112	1,112	1,469	1,031	155,6	57,5	155,6	57,5	121,1	121,1	113,1	

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*The designation of the parameters are given in Figs. 1 and 2; bond lengths, Å; angles, deg.

†The data on the STO-3G calculations of the structures of (I, II, IV) were taken from [8, 9].

‡The parameters α and β relate to the C—H bonds on the same side of the plane of the ring as the heteroatom—hydrogen bond [in the molecules of (I, IV)] or as the solvent molecule [in complexes (V-VIII)].

Energy minima corresponding to the aziridine-hydroxonium cation (IX), ethylene oxide—hydroxonium ion (X), aziridine—ammonium ion (XI), and protonated ethylene oxide—ammonia (XII) complexes were not found. The STO-3G calculations cannot, of course, be used as the basis for conclusions about the absence of the above-mentioned complexes in the gas phase. At the same time it should be noted that the stable complex $(H_2OH...NH_3)^+$, which is to some degree the analog of systems (IX, XII), was not found during quantum-chemical investigation of the ammonia—proton—water system, using a two-exponent basis set [7]. In solutions, however, compounds (IX-XII) may also exist in addition to the complexes (V-VIII), since the solvation may increase their stability. The results from calculations on the parameters of the molecules of (I-IV) and of the complexes (V-VIII) are given in Figs. 1 and 2 and Tables 1 and 2. According to the calculated data, the principal geometric characteristics of the three-membered rings in the complexes (V-VIII) occupy an intermediate position between the corresponding values for the protonated and unprotonated forms of aziridine and ethylene oxides. The reactivity of the complexes (V-VIII) must also, therefore, be lower than in

TABLE 3. The Charges on the Methylene Groups in Compounds I-VIII, XIV, XV, Determined by the STO-3G Method, and the Potential Barriers for Their Reactions with Ammonia

Compound	q_{CH_2}*	E_a, kJ/mole	
		determined by MINDO/3	calculated by means of Eq. (7)
I	0,0727	198,9 [1, 2]	194,1
II	0,1038	167,9 [1, 2]	166,3
III	0,3364	66,2 [1, 2]	52,4
IV	0,3969	34,8	38,8
V	0,2581		77,3
VI	0,2296	87,5 [1, 2]	89,0
VII	0,2817		68,7
VIII	0,2436	72,0 [1, 2]	83,0
XIV	0,2192		93,8
XV	0,1911		107,8

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*In electron charge units.

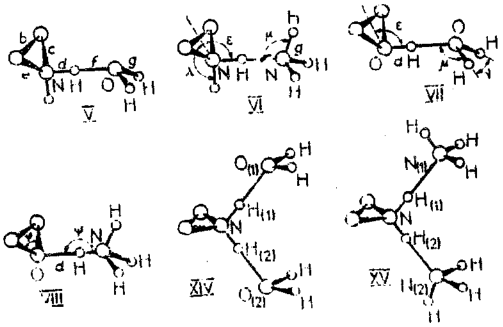


Fig. 1

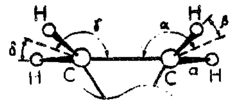


Fig. 2

Fig. 1. The conformations of the complexes, calculated by the STO-3G method.

Fig. 2. The common fragment of the three-membered rings in the complexes.

compounds (III, IV) but higher than in the rings (I, II). The calculated heats of stabilization of the complexes vary appreciably in the series of (V-VIII) but are large in all cases.

Earlier we reported the results from MINDO/3 calculations on the gas reactions (1-6) of compounds (I-IV) and also the protonated aziridine–ammonia (VI) and ethylene oxide–ammonium ion (VIII) complexes with ammonia [1, 2]:

$$I + NH_3 \xrightarrow{\text{slow}} {}^{\delta-}NHCH_2CH_2NH_3{}^{\delta+} \xrightarrow{\text{fast}} NH_2CH_2CH_2NH_2, \quad (1)$$

$$II + NH_3 \xrightarrow{\text{slow}} {}^{\delta-}OCH_2CH_2NH_3{}^{\delta+} \xrightarrow{\text{fast}} HOCH_2CH_2NH_2, \quad (2)$$

$$III + NH_3 \longrightarrow NH_2CH_2CH_2NH_3{}^+, \quad (3)$$

$$IV + NH_3 \longrightarrow HOCH_2CH_2NH_3{}^+, \quad (4)$$

$$VI + NH_3 \xrightarrow{-NH_3} NH_2CH_2CH_2NH_3{}^+, \quad (5)$$

$$VIII + NH_3 \xrightarrow{-NH_3} HOCH_2CH_2NH_3{}^+. \quad (6)$$

The structural parameters of the associates (VI, VIII) obtained by the MINDO/3 method are similar to the data from calculations in the STO-3G basis set. It is known, however, that in a number of cases the MINDO/3 method describes the hydrogen bond unsatisfactorily [10]. As a result the method proved unsuitable for calculation of the characteristics of the transition states in the reactions of the complexes (V, VII) with ammonia. The results from calculations with the STO-3G basis set were therefore used during assessment of the reactivity of these and certain other associates.

The Mulliken charges at the carbon atoms of the three-membered rings and the total charges on the methylene groups in them (a_C and a_{CH_2} respectively), determined by the STO-3G method, vary significantly in the series of systems (I-VIII) and can be used as reactivity indices. We examined the relationships between the charges q_C or q_{CH_2} for compounds I-IV, VI, VIII and the potential barriers (E_a) for the amination of these systems (1)-(6), calculated by the MINDO/3 method. The size of the potential barrier for reaction (4) given here (Table 3) differs somewhat from the value reported earlier [2], since the parameters for the transition state of (XIII) in this process were refined in the present work (see the section on the computation procedures).

A good linear a_C–E_a correlation was not obtained for the six reactions given above (correlation coefficient r = -0.83), but a satisfactory q_{CH_2} – E_a was observed (r = -0.96). Thus, it was possible to obtain an approximate estimate of the potential barriers for the amination reactions from the charges on the methylene groups of the substrates. For this purpose we used the empirically selected linear correlation between the charges q_{CH_2} and the logarithms of the potential barriers (r = -0.98):

$$E_a = \exp(-4.9692 q_{CH_2} + 5.6298), \tag{7}$$

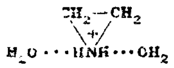
From Table 3 it is seen that the values of the potential barriers calculated by means of Eq. (7) are fairly close to the values obtained by direct calculation. This shows that the equation is suitable for determining the reactivity of the investigated systems. According to the data in Table 3, all four complexes (V-VIII) exhibit fairly high reactivity in reactions with ammonia. Moreover, ammonolysis is possible in the (IX-XII) systems, which (as mentioned above) may also be present in the solutions. In order to solve the question as to which of the associates are the main participants in the reaction it is necessary to determine their relative concentrations in the solution. Since the free energy of reaction (8) in aqueous solution amounts to -52.3 kJ/mole [11] and since the basicities of oxirane and water are close, it must be supposed that the concentrations of the hydroxonium ion and also of the protonated ethylene oxide in the aqueous ammonia solutions are negligibly small compared with the concentration of the ammonium ion.

$$H_3O^+ + NH_3 \longrightarrow NH_4^+ + H_2O \tag{8}$$

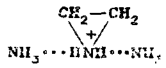
The concentrations of the associates (VII, X, XII) must be correspondingly small in comparison with the complex (VIII). Since the difference in the reactivities of the five complexes is not very large [cf. the E_a values for the reactions of the associates (VII) and (VIII) with ammonia, Table 3], the main reagent in the amination of ethylene oxide under real conditions is in all probability the ethylene oxide–ammonium ion complex (VIII).

It is more difficult to make analogous estimates for the reactions with aziridine. On account of the low concentration of the hydroxonium ion the amount of particles (IX) in the solution is undoubtedly negligibly small compared with the complexes (V, VI, XI), the concentrations of which are clearly similar in order of magnitude. Since the pK_a values for the conjugate acids in water are somewhat higher for ammonia than for aziridine (9.3 [12] and 8.0 [3]), it can be supposed that the concentration of the ammonium ion–aziridine complex (XI) in the aqueous ammonia solution is higher than the concentration of the associate (VI), while the latter in turn clearly exceeds the concentration of the complex (V) [since, according to data in Table 1, the heat of stabilization of the complex (VI) is larger in absolute value than that of system (V)]. At the same time the reactivity in amination reactions decreases in the following order (Table 3): V > VI > XI. In our opinion, the main reacting particles in the reactions of aziridine with ammonia are the associates (VI, V), formed by the protonated aziridine with a solvent molecule, since they are present in the solution in sufficient quantities, and their reactivity must be perceptibly higher than that of the complex of aziridine with the ammonium ion (XI).

It must also be borne in mind that the protonated aziridine is capable of forming at least two hydrogen bonds with the solvent molecules. In the present work we considered two such complexes (XIV, XV) (Figs. 1 and 2, Tables 1 and 2).



XIV



XV

Their reactivity is somewhat lower than that of the associates with one solvent molecule (Table 3). Without calculating the free energies of complex formation it is difficult to conclude which of the complexes (with one or two solvent molecules) is present in the solution in sufficient quantities. In any case, complex formation with one solvent molecule already satisfies the capacity of the protonated aziridine to act as a hydrogen bond donor to a significant degree.

The foregoing shows that the following can act as reacting particles in acid-catalyzed liquid-phase amination reactions: 1) The protonated molecules of the three-membered rings attached to solvent molecules by strong hydrogen bonds; 2) the molecules of the three-membered rings included in the first solvate shell of ammonium or hydroxonium ions. In the latter case the transfer of the proton to the ring heteroatom, the formation of the carbon atom—nucleophile bond, and the opening of the ring take place synchronously. The above-mentioned processes correspond to two types of acid catalysis, where the first type is more effective than the second. The second type of catalysis can be realized if the concentration of associates of the first type in the solution is negligibly small. As shown above, the reaction with aziridine is catalyzed by a mechanism of the first type, while the reaction with ethylene oxide is catalyzed by a mechanism of the second type. Generally speaking, acid catalysis can be realized even if the molecule of the ring enters the second or third solvate shell of NH_4^+ or H_3O^+, since in this case synchronous transfer of the proton along the chain is possible. However, since elongation of the chain leads to a rapid increase in the energy expenditures [13], this mode of catalysis probably does not play a significant role.

COMPUTATION PROCEDURES

The nonempirical calculations were performed by means of the GAUSSIAN-70 program [14]. During the calculations the optimization of the structure was considered complete if the decrease in the calculated total energy of the system in the next cycle of optimization of the geometric parameters was not greater than 5.10^{-5} au. During the calculation of the characteristics of the complexes V-VIII, XIV, XV certain limitations were imposed on their geometric structure. It was assumed that the heteroatoms of the solvent molecules and all the atoms of the apical groups of the rings lie in the bisecting plane of the angle φ (Fig. 1). The angle φ was taken as equal to 180°. For each complex it was assumed that the lengths of all the C—H bonds, all the angles μ, and the lengths of all the N—H or O—H bonds in the solvent molecules were identical. It was also assumed that the ammonia molecules in the complexes retain the local symmetry axis. During calculation of the structures of the complexes containing two solvent molecules it was assumed that $\varepsilon = \lambda$, $d = e$, and N^1H^1 (or O^1H^1) $= N^2H^2$ (or O^2H^2) $= f$. The calculations showed that the structures of all the complexes have a plane of symmetry. One conformer was found for each of the associates V-VIII, XV, and three conformers for the complex (XIV). The characteristics of the most stable of the latter are given in Figs. 1 and 2 and in Tables 1 and 2.

The MINDO/3 calculations on reaction (4) were carried out in the reaction coordinate mode by a procedure similar to that described in [2]. The obtained structure of (XIII) was identified as the transition state. (The Hessian for this structure had only one negative eigenvalue.) To identify the transition state we used a program written by V. A. Pichko (Rostov State University).

The structure of (XIII) differs little from that reported earlier [2], but its NH_3 group is rotated by 60° in relation to the local rotation axis. The calculated enthalpy of formation for the transition compound (XIII) is 610.8 kJ/mole.

The authors are grateful to M. V. Bazilevskii for discussing the results.

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MECHANISM OF AMINATION OF AZIRIDINES AND OXIRANES.

4.* QUANTUM-CHEMICAL INVESTIGATION OF THE EFFECT OF THE POLAR SOLVENT

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UDC 547.717:541.124'12.038.2

The effect of nonspecific solvation on the mechanism of the amination of three-membered rings was investigated by the MINDO/3 quantum-chemical method and by the solvaton model.

The energy of nonspecific solvation is determined primarily by electrostatic interactions between the self and induced charges of the solvate and the solvent. Interactions of this type can be calculated by means of the solvation model of Germer [2], in which the solvent is modelled by a set of point charges (solvatons) surrounding the dissolved molecule, and it is assumed that each atomic center of the molecule induces one solvaton with a charge having a sign opposite to the charge of the atom. We used the version of the solvaton model proposed in [3]. This model, realized within the framework of the CNDO/2 method, was calibrated for a set of neutral and positively charged molecules similar in structure to the calculated systems (see the computation procedure section). Since the protonated aziridine–ammonia (I) and ethylene oxide – ammonium ion (II) complexes are some of the most likely participants in amination reactions, calculation of the energy parameters of the reactions of these associates with ammonia (1,2) with allowance for electrostatic solvation makes it possible at a qualitative level to study the effect of both general and specific solvation effects.

I II

$$\mathrm{I} + NH_3 \xrightarrow{-NH_3} NH_2CH_2CH_2NH_3^+ \qquad (1)$$

$$\mathrm{II} + NH_3 \xrightarrow{-NH_3} HOCH_2CH_2NH_3^+ \qquad (2)$$

Here the specific solvation is taken into account by MINDO/3 calculation in the supermolecule approach through inclusion of the solvent molecule in the reaction system, and the heats of interaction of the solvate with the polar solvent medium are calculated by means

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*For Communication 3, see [1].

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