Mechanism of interaction of diallylmethylamine and its protonated and quaternary forms with their own radicals in solvent

L. M. Timofeeva, Yu. A. Vasilieva, N. A. Kleshcheva, and D. A. Topchiev*

A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 117912 Moscow, Russian Federation. Fax: +7 (095) 230 2224. E-mail: ips@tips.aha.ru

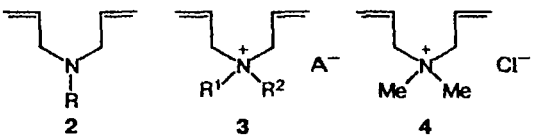
The potential energy profiles of reactions of diallylmethylamine and its protonated and quaternary forms with their own radicals were calculated by the semiempirical MNDO-PM3 method taking into account electrostatic solvation effects in the framework of the self-consistent reaction field model. The reactions studied simulate chain propagation and chain transfer to monomer in radical polymerization of the above monomers in dilute solutions with different dielectric permittivities of the solvents. The conformations of monomers in the gas phase and in solvent were studied. It was found that protonation and quaternization lead to successive increase in the activation energy of mobile allyl hydrogen atom abstraction and to increase in the difference between the activation barriers to competing reactions of chain transfer and propagation. The results obtained make it possible to predict the conditions of the synthesis of high-molecular-weight polymers based on diallylamine monomers. The mechanisms of reactions studied are discussed.

Key words: diallylmethylamine, diallylmethylammonium, radical polymerization, chain propagation, degradative chain transfer, solvent, free electrostatic solvation energy, potential energy profile, activation energy, quantum-chemical calculations, MNDO-PM3 method.

The problem of radical polymerization of allyl monomers has long been studied.[1–7] It was established that polymerization of these compounds is to a great extent controlled by the reaction of degradative chain transfer to the monomer occurring with abstraction of the α-hydrogen atom of the allyl group of the monomer by the propagation radical to form a stable low-reactive allyl radical. This results in the kinetic chain termination, formation of low-molecular weight oligomeric products, and complete inhibition of polymerization because of the low reactivity of the allyl radical that formed.[1–7]

It was established in the studies of polymerization kinetics that the polymerization rate of allyl monomers and the molecular weight (MW) of low-molecular weight oligomers substantially increase in complex-forming and acidic media, *viz.*, they increase as proton-donor properties of acid (solvent) and the basicity of allyl monomers increase.[3–7] This effect is explained by an increase in the strength of the α-C—H bonds in the allyl group upon protonation (or complexation) and by increase in the reactivity of allyl radical, *i.e.*, by partial transformation of degradative chain transfer into effective one in this type of media.[3–7]

All said above is also true for compounds of the diallyl series including diallylmethylamine (1) and monomers of the diallylamine series (2).[6–8] Only on going to quaternary forms of compounds 2, *viz.*, salts of disubstituted *N*,*N*-dialkyl-*N*,*N*-diallylammonia (3), the degradative chain transfer to monomer can be inhibited to a great extent and converted into effective chain transfer to monomer,[9,10] which makes it possible to solve thus the problem of synthesizing high-molecular weight products based on monomers of the type 3 at relatively high polymerization rates.[10,11]



2 3 4

R = H, Me, CMe_3;
$R^1 = R^2$ = Me, Et or $R^2 = CH_2COOCHMe_2$;
A = Cl, Br, BF_4

At the same time, the mechanisms of several phenomena observed in the processes under consideration and the role of protonation and, especially, quaternization of diallylamine in the reduction of the competing ability of the reaction of abstraction of the α-hydrogen atom of allyl group remain unclear. In addition, the mechanism of the conversion of degradative chain transfer to monomer into effective chain transfer to the monomer, *i.e.*, of the passage from the stable allyl radical to the reactive form, has not been studied.

The aim of this work was to consider the first issue, *viz.*, to study addition reactions of the radical to the double bond of the monomer and abstraction reactions of the mobile hydrogen atom of the allyl group of the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 865—872, May, 1999.

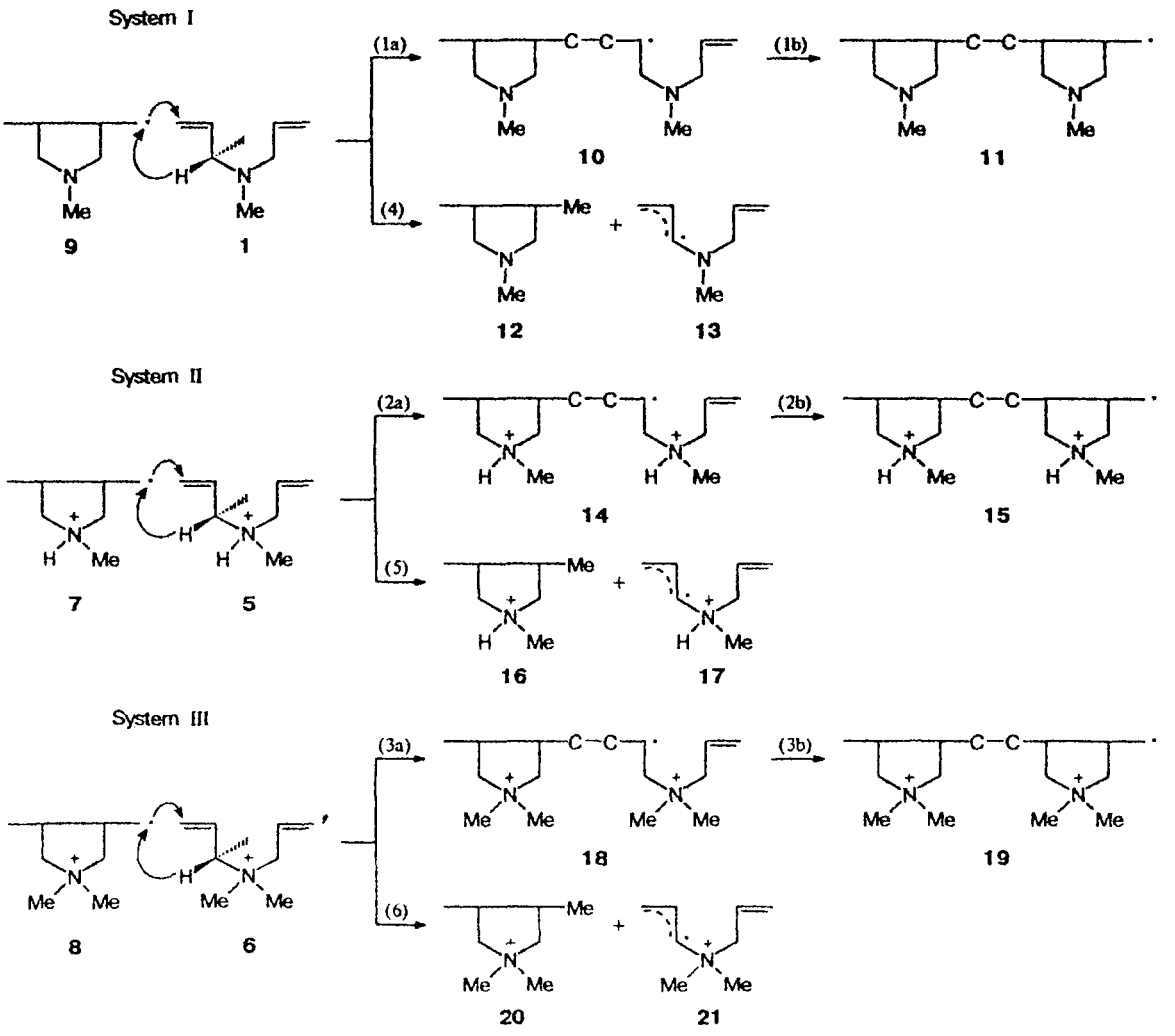
1066-5285/99/4805-0856 $22.00

monomer by radical, that simulate the chain propagation and chain transfer to the monomer upon radical polymerization of compound **1** and its protonated and quaternary forms. This issue is of interest from theoretical point of view as a problem of structural chemistry and, at the same time, can be a key problem for the search of the conditions of production of high-molecular weight polymers based on monomers **1** and **2**.

It was established by elemental analysis[12] and by NMR and ESR spectroscopy[13–15] that the addition of radical to the "tail" of one of the allyl groups of the monomer followed by fast intramolecular cyclization and the formation of a five-membered cycle is the limiting stage of reactions of the monomers of the series **2** and **3** with various radicals and in different solvents. The acyclic radical form has not been detected to date[13,14] because of extremely high cyclization rate (at 25 °C). No allyl radicals formed upon abstraction of the mobile hydrogen atom were also detected in the experiments;[13,14] however, the ESR spectrum of a similar radical at 77 K was first recorded in the studies of the reaction of allyl alcohol with a radical initiator.[16] In addition, signals of end methyl and vinyl groups indicating the occurrence of the reactions of chain transfer to the monomer were recorded in ^1H and ^{13}C NMR spectra of a polymerization product of diallyldimethylammonium chloride (**4**).[9]

Taking into account the aforesaid, we studied three reaction systems (I—III) simulating the elementary reactions of chain propagation and chain transfer to the monomer upon polymerization of compound **1**, its protonated form, *viz.*, diallylmethylammonium (**5**), and the diallyldimethylammonium cation (**6**) (Scheme 1). System I was used to consider the elementary reactions occurring upon polymerization of amine **1** in the bulk of monomer and in organic solvents of different polarity (the solubility of compound **1** in water does not exceed 8% under normal conditions). Using system II, an ideal limiting case of the interaction between cations of a completely protonated monomer and radical in highly

Scheme 1



dilute acidic solutions of different polarity was simulated (the effect of anionic residue of the acid was not considered). Using system III, we studied elementary polymerization reactions of salt **4** in highly dilute solutions where its cation **6** is free solvated and isolated from the influence of solvated Cl^- anion in solution.

Calculation procedure

Calculations of the gas-phase reactions were performed by the MNDO-PM3 method[17] with full geometry optimization using the MOPAC-6 program, while radical forms were calculated in the framework of the UHF approximation. Zero-point vibrational energy corrections were ignored. The inductive effect of the N atom in the series of monomers **1**, **2**, **5**, and **6** was also assessed by the AM1 method.[18] Previously, the PM3 and AM1 methods were used to calculate the potential energy profiles and surfaces, as well as the entropy factors of analogous reactions, *e.g.*, the radical dimerization of ethylene and chain transfer to monomer,[19] and dimerization of several acrylates.[19,20] Comparison of the results obtained for these systems using semiempirical and various *ab initio* methods has shown[19] that the former provide semiquantitative agreement with experimental data.[19,20]

The potential energy profiles were calculated along the reaction coordinate, *i.e.*, along the distance l_1 between the reacting carbon atom of the radical and the terminal atom of the double C=C bond of the monomer (Fig. 1, *a*) and along the distance l_2 between the reacting carbon atom of the radical and the mobile hydrogen atom of the allyl group of the monomer (Fig. 1, *b*). After reaching a transition state (TS) whose geometry was also controlled by special search using the MOPAC-6 program, the TS energy was additionally scanned through the torsion angle of rotation (φ) of one allyl group about the other one in the monomeric fragment and then the structure of the found TS conformer of minimum energy was refined in a narrow region of the l_1 or l_2 reaction coordinates in the vicinity of the saddle point.

Calculations of the electrostatic solvation effects were performed using the SOLPAC program,[21] which employs the self-consistent reaction field (SCRF) approximation[22] and semiempirical methods at the stage of quantum-chemical calculations. Trial calculations of several ammonium (including pyrrolidinium and *N*-methylpyrrolidinium) and oxonium ions showed that the experimental values of the sums of electrostatic and specific contributions to the free hydration energy are reliably reproduced in the framework of the SOLPAC procedure.[21] The small contribution of specific solvation due to hydrogen bonding to the free hydration energy of ammonium ions is in agreement with the experimental data[23].

Full optimization of geometric parameters of the ground state of monomer **5** performed with consideration of the solvent effect showed that the enthalpy of formation of **5** decreases slightly (by 0.1 kcal mol^{-1}) as compared to the value obtained using the gas-phase parameters. However, these calculations appeared to be time consuming (about 6 h of computing time). At the same time, it was reported[21] that the use of gas-phase parameters in calculations performed taking into account medium effects should not introduce considerable errors. Therefore calculations with consideration of solvent effects were carried out using optimum geometric parameters of the reagents and TS fragments calculated for the gas phase. In this case the TS structure was partly optimized along the l_1, l_2, and φ reaction coordinates with inclusion of solvent effects

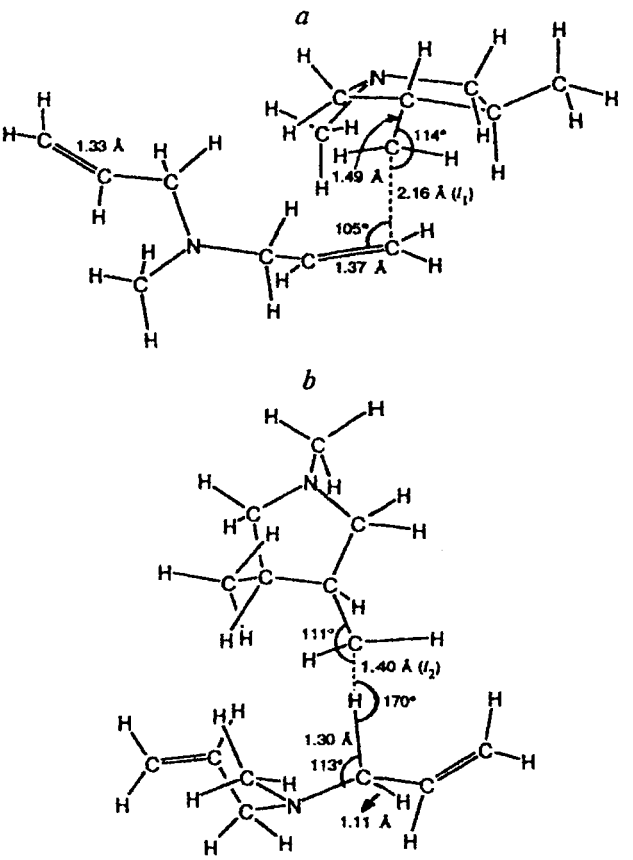


Fig. 1. Structures of transition states of reactions (1a) and (4) in Scheme 1: addition of radical to the double bond (*a*) and abstraction of α-hydrogen atom of the allyl group (*b*).

by scanning through a specified range of the values of these gas-phase parameters, which, as a rule, did not change on taking account of electrostatic solvation.

As is known, the free solvation energy (ΔG_S) can be represented as the sum of electrostatic (ΔG_{el}) and specific (ΔG_{sp}) contributions and also the overall contribution (ΔG_V) of the dispersion, van der Waals, and cavitation free energies (ΔG_V can be considered as a nonelectrostatic contribution), dependent, in particular, on the volume of the cavity (V) occupied by a solute molecule (ion) in the medium[21]:

$$\Delta G_S = \Delta G_{el} + \Delta G_{sp} + \Delta G_V. \qquad (7)$$

In the case of equilibrium solvation the activation energy of reaction in solution ($E_{0,S}$) is determined by the sum of the activation energy in vacuum (E_0) and the difference between the free solvation energies of the TS ($\Delta G_S^{\neq}$) and the reagents (ΔG_S^r):

$$E_{0,S} = E_0 + \Delta(\Delta G_S),$$

$$\Delta(\Delta G_S) = \Delta G_S^{\neq} - \Sigma \Delta G_S^r.$$

Taking into account the reported data,[21,23] for the reactions considered the ΔG_{sp} term in Eq. (7) can be neglected. We did not assess the contribution of the ΔG_V free energies.

Obviously, this introduces no considerable error when comparing the energetics of the chain propagation and chain transfer reactions for the same reaction system, because the initial reagents remain the same, the structures of the TS are almost identical, and the volumes of the cavities for the transition states of chain propagation and chain transfer, according to our calculations, are equal for each of the systems I—III. Elimination of the ΔG_V terms can introduce a small error when determining the relative energetics of two reactions for systems I and III or systems II and III (the volumes of the cavities occupied by the reagents and the TS in systems I and II are virtually equal). The maximum difference in the volumes of the cavities due to the introduction of Me groups into the reagents and TS is small and approximately constant (according to our calculations, it is 14 to 16% when comparing the reagents (or the TS) for systems I and III). Taking into account that, according to the experimental data (see Ref. 21 and references cited therein), the introduction of one Me group into the molecules of cyclic or aliphatic hydrocarbons increases the positive hydration energy of the hydrocarbons (which is, obviously, determined by the ΔG_V term) by no more than 0.3—0.4 kcal mol^{-1} and that the effect of the introduction of two Me groups is, as a rule, less than the additive effect (no more than 0.6 kcal mol^{-1}), we get that the maximum error will be no more than 0.2 kcal mol^{-1} when comparing the $E_{0,S}$ values for the reactions occurring in different systems. The error of the determination of the $E_{0,S}$ absolute value is expressed by the $\Delta G_V^* - \Sigma\Delta G_V^r$ term, where ΔG_V^* is the free nonelectrostatic solvation energy of the TS and ΔG_V^r is the sum of the contributions of the free nonelectrostatic solvation energies of the reagents. Taking into account that introduction of one CH_2 group into a hydrocarbon molecule increases the positive energy of its hydration by approximately 0.2 kcal mol^{-1},[21] it can be shown that the desired error for the systems under consideration will be no more than 1 kcal mol^{-1}. Thus, the $E_{0,S}$ values were calculated using the equation

$$E_{0,S} \approx E_0 + (\Delta G_{el}^* - \Sigma\Delta G_{el}^r), \qquad (8)$$

where ΔG_{el}^* is the free electrostatic solvation energy of the TS and $\Sigma\Delta G_{el}^r$ is the sum of the contributions of the free electrostatic solvation energy of the reagents.

It is obvious that the length of the macroradical chain should not affect the activation energy of the reactions under study (in contrast to its effect on the entropy factor)[19]; hence the results of calculations of the activation barriers to the above reactions can be compared with the kinetic data for actual polymerizing systems in the linear region of small monomer conversions (up to 2—5%).

Results and Discussion

Reagents

According to the results listed in Table 1, the free electrostatic solvation energies of cationogenic monomers and radicals are well reproduced by the computational method used. Introduction of a Me group in positions 3 and 4 of *N*-methylpyrrolidinium causes a decrease in the ΔG_{el} value of the 1,3,4-trimethylpyrrolidinium radical (**7**), whereas introduction of the second Me group in position 1 of radical **8** leads to a further decrease in the ΔG_{el} value by 4 kcal mol^{-1}. The ΔG_{el} values of monomeric forms **5** and **6** are smaller than those of the corresponding radicals **7** and **8** because of the more branched structure of the former.

Table 1. Free electrostatic solvation energies (ΔG_{el}/kcal mol^{-1}) of cationogenic reagents[a]

Compound	ΔG_{el} (calc.)	$\Delta G_{el} + \Delta G_{sp}$[b]
Pyrrolidinium	61.8[c]	62.8
N-Methylpyrrolidinium	56.0[c]	56.2
7	54.9	
8	50.8	
5	52.2	
6	48.7	

[a] $\varepsilon = 80$.
[b] Estimates of experimental values were taken from Ref. 21.
[c] Calculated using the SOLPAC program.[21]

In the course of calculations we studied possible spatial conformations of the monomers, obtained by rotating one allyl group about the other. Several stable conformations of each monomer can be found both in the gas phase and in solvent ($\varepsilon = 80$), *viz.*, three conformations of monomer **1** (*cis*-, *gauche*-, and *trans*-conformers whose heats of formation (ΔH_f) differ by 1.2 kcal mol^{-1}) and monomer **5** and two conformations of monomer **6**. These results are in agreement with the data obtained by steam chromatography, according to which there is a possibility of separating compound **2** into several stereoisomers[24] using $AgNO_3$ (this part of the study is of special interest and requires additional investigations). Calculations of activation energies were performed for conformers with minimum ΔH_f values.

Reactions of addition to the double bond — chain propagation

The energy diagrams of the reactions of free-radical addition to the double bond in solvent ($\varepsilon = 80$) are shown in Fig. 2. According to calculations, an open form of the dimeric radical is the stable product formed in the limiting stage (a) both in the gas phase and in solvent. An early TS, in which the structure of the reacting fragments is close to that of the initial reagents, is observed at this stage (see Fig. 1, *a*), which is in agreement with general concepts of free-radical addition[25] and, in particular, with the results of *ab initio* calculations of the TS structure of ethylene radical dimerization (see Ref. 26 and references cited therein). Structural similarity of the TS and reagents is in agreement with the high exothermicity of reactions (1a)—(3a) obtained in calculations (see Fig. 2); the end products of all reactions following the routes (1)—(3) are more thermally stable cyclic dimeric propagation radicals **10**, **14**, and **18**, respectively, formed as a result of intramolecular cyclization (see Fig. 2).

Changes in the activation energies of chain propagation reactions (1a)—(3a) are small; they correlate with

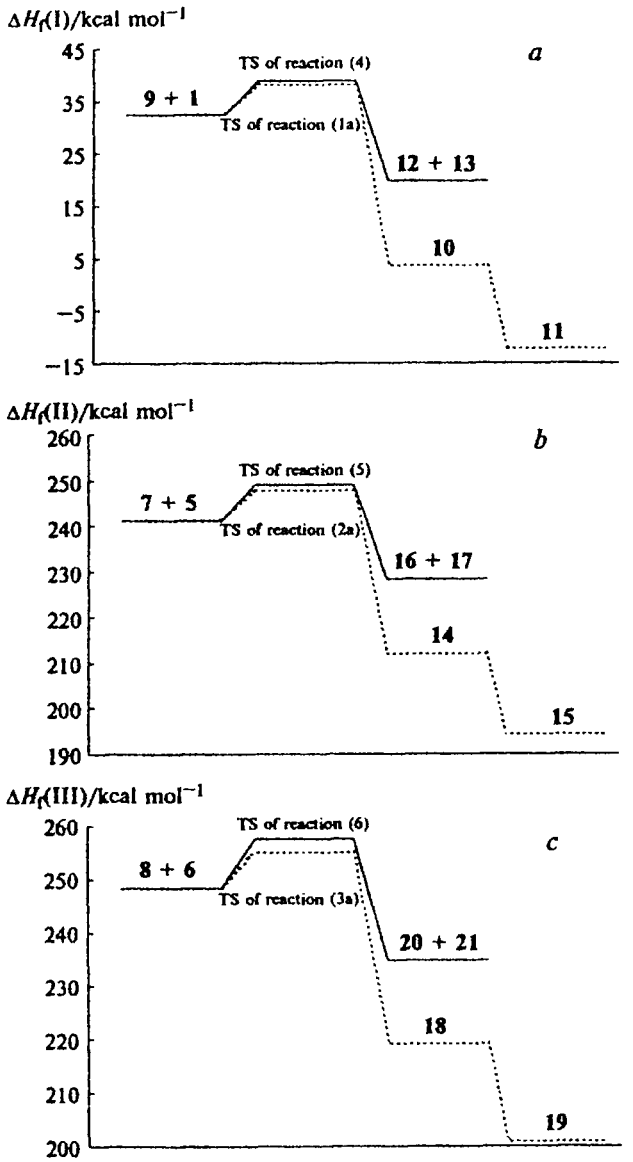


Fig. 2. Energy diagrams of the reactions of addition of radical to the double bond (dashed line) and abstraction of the α-hydrogen atom of the allyl group (solid line) for systems I (*a*), II (*b*), and III (*c*).

electronic and energy characteristics of interacting frontier π-orbitals (FMO) and are controlled primarily by the energy difference between these orbitals (Table 2), which is in agreement with the concepts of radical addition.[25] A slight increase in the $E_{0,S}$ energy of the reaction of addition to the double bond observed upon protonation and quaternization (the difference between the $E_{0,S}$ values of reactions (3a) and (1a) or (2a) can be 0.2 kcal mol^{-1} smaller if calculations of solvation effects are performed taking into account the ΔG_V terms, see above) is associated with increase in the difference between the HOMO energies of radical and monomer. This is due to a higher

Table 2. Calculated activation energies (E_0, $E_{0,S}$/kcal mol^{-1}) of chain propagation reactions and correlations with π-electron characteristics (E_{FMO}, E_π/eV) of interacting frontier molecular orbitals (FMO)

Reaction	E_0, vacuum	$E_{0,S}$ ε = 80	$E_{0,S}$ ε = 25	E_{FMO} [a]	E_π [b]
(1a)	5.5	5.8	5.8	0.52	0.71
(2a)	45.2	6.5	7.4	1.44	0.24
(3a)	44.5	6.8	7.6	1.42	0.20

[a] The energy difference between the interacting FMO; ε = 80.
[b] Estimate of the π-electron energy of the interaction between the FMO; calculated in the framework of perturbation theory (see, *e.g.*, Ref. 25); the β resonance integral was assumed to be equal to 1 eV; ε = 80.

stabilization of monomeric forms upon protonation or quaternization as compared to radicals. The increase in the activation energies of the reactions of cationogenic forms upon decrease in the dielectric permittivity of the medium is due to the decrease in the free solvation energy in less polar media, which manifests itself to a greater extent for bulky structures of TS.

No experimental data on the activation energies of the reactions considered are available. The rate constant for chain propagation in the polymerization of compound **4** was reported, *viz.*, $k_p = (2.0\pm0.2)\cdot10^3$ L mol^{-1} s^{-1} at a concentration of 0.75 mol L^{-1} and T = 25 °C.[27] Using the experimental value of the entropy (preexponential) factor for ethylene polymerization ($1.9\cdot10^7$ L mol^{-1} s^{-1}),[26] it is possible to estimate the activation energy (E_a) at 25 °C, which is equal to 5.5 kcal mol^{-1}. Comparison with this value is somewhat incorrect since it is only a rough estimate. At the same time, it was mentioned above that taking account of the ΔG_V terms may lead to a decrease in the calculated absolute values of $E_{0,S}$ of reaction (3) by a value of $|\Delta G_V^{\ddagger} - \Sigma\Delta G_V| \approx 1$ kcal mol^{-1}. However, the application of temperature corrections should increase the $E_{0,S}$ value by a value not larger than RT (*i.e.*, 0.6 kcal mol^{-1} at 25 °C).* On the whole, the calculated absolute values of

* The height of the potential barrier (E_0) calculated with inclusion of zero-point vibrational energy corrections and the E_a value obtained experimentally from the Arrhenius equation are related to the considered type of reactions as follows[28]:

$$E_a = E_0 - RT^2 \cdot d\{\ln[Q^{\ddagger}/(Q_{mon} \cdot Q_{rad})]\}/dT + RT,$$

where $Q^{\ddagger}$, Q_{mon}, and Q_{rad} are the molecular partition functions over states for the TS, the monomer, and the radical, respectively. The second and third terms in this expression are temperature corrections for the E_0 value. For the reaction of addition of ethyl radical to ethylene (calculations by the QCISD(T)/6-311G* method), the temperature correction for 323 K calculated at a HF/6-31G* level of theory was 1.8 kJ mol^{-1} (0.4 kcal mol^{-1}), *i.e.*, somewhat less than the corresponding RT value (0.6 kcal mol^{-1}).[26]

$E_{0,S}$ of reactions (1a)—(3a) are in agreement with experimental and theoretical data on the activation energy of addition of a hydrocarbon radical to the double C=C bond. The experimental $E_{0,S}$ value for the well-studied reaction of ethylene polymerization is 7.3 kcal mol^{-1} at 50 °C (see references cited in Ref. 26), whereas the $E_{0,S}$ values for ethylene dimerization calculated by the *ab initio* QCISD(T)/6-311G* method with inclusion of zero-point vibrational energy correction calculated at the HF/6-31G* level of theory without considering solvent effects are 7.4 and 7.8 kcal mol^{-1} without and with temperature correction (+0.4 kcal mol^{-1} at 50 °C), respectively.[26] It should be noted that the activation energy calculated at lower levels of theory (*e.g.*, by the HF/3-21G and HF/6-31G* methods) without inclusion of electron correlation appeared to be overestimated (8.9 and 12.2 kcal mol^{-1}, respectively).[26]

Abstraction of the mobile proton — chain transfer to monomer

A characteristic collinear structure of TS (see Ref. 29 and references cited therein) was obtained for the reactions of proton abstraction (see Fig. 1, *b*). According to calculations, the activation energies of the reactions of proton abstraction considered above are higher than those of corresponding alternative reactions of addition to the double C=C bond (Table 3, see Fig. 2), which is in agreement with the experimental data on the activation energies of the reactions of chain propagation and abstraction of the mobile proton in the radical polymerization of allyl acetate.[1] Charge separation in TS observed for reactions (4)—(6) is a specific feature of this type of reactions.[29] Transition states of reactions (5) and (6) are solvated better than those of the alternative reactions (2a) and (3a), respectively (Table 4), which is likely due to a higher polarization of the charges. Addition of the second Me group to the N atoms in the TS of reactions (3a) and (6) leads not only to a regular decrease in the absolute values of ΔG_{el}^{*} of these structures as compared to the corresponding values for the TS of reactions (2a) and (5), but also to a decrease in the difference between the free solvation energies of TS and corresponding initial reagents; this difference is a relative quantity determined by structural and electronic parameters of the systems and is independent explicitly of the number of Me substituents, in contrast to the absolute free energies (see Table 4).

It seems likely that the increase in the barriers to the reactions of abstraction of the mobile proton in the series (4)—(6) is determined by two factors. The first factor is the strength of the α-C—H bonds of allyl groups, which increases upon protonation or quaternization of the amines (see Table 3). Selected energy and structural characteristics of monomers **1**, **5**, **6**, and **2** calculated by the AM1 method are listed in Table 5. In this case the AM1 method is more illustrative in reproducing the changes in the bond lengths and

Table 3. Calculated activation energies (E_0, $E_{0,S}$/kcal mol^{-1}) of the reactions of abstraction of the α-hydrogen atom and the energies (E_b/eV) of the α-C—H bonds

Reaction	E_0, vacuum	$E_{0,S}$		E_b*
		ε = 80	ε = 25	
(4)	6.1	6.4	6.4	−12.55
(5)	52.8	7.7	9.0	−12.69
(6)	52.4	9.2	10.1	−12.71

* The total two-center energy of the α-C—H bond.

Table 4. Absolute and relative free electrostatic solvation energies (ΔG_{el}/kcal mol^{-1}) of transition states of reactions of cationogenic forms[a]

Reaction	$-\Delta G^{*}_{el}$	$\Delta G^{*}_{el} - \Sigma\Delta G_{el}$[r] [b]
(2a)	145.8	−38.7
(3a)	137.1	−37.6
(5)	152.2	−45.1
(6)	142.7	−43.2

[a] ε = 80.

[b] Difference between the free electrostatic solvation energies of transition state and the reagents.

electronic structure observed upon protonation and alkylation in the series of amines considered. From the data in Table 5 it can be seen that protonation or quaternization causes jumpwise changes in the characteristics of the systems as compared to the nonionized amines **1** and **2**. Most likely, the formation of the bond with the vacant electron pair leads to a decrease in the inductive effect of the N atom and, hence, to a weakening of the C—N bonds of allyl groups and, correspondingly, to a strengthening of α-C—H bonds. Alkylation itself introduces no considerable changes.

The analysis performed shows that the increase in the activation energy of abstraction of a hydrogen atom on going from the protonated amine to the quaternary form is due to solvation effects caused by introduction of a Me substituent, which leads not only to an absolute, but also to a relative decrease (compared to solvated

Table 5. Structural and energy characteristics of monomers calculated by the AM1 method

Compound	$-E_b$(α-C—H) /eV[a]	P(α-C—H)[b]	$-E_b$(α-C—N) /eV[a]	l(α-C—N) /Å[c]
2	11.97	0.946	14.79	1.452
1	11.97	0.948	14.66	1.457
5	12.07	0.952	12.99	1.507
6	12.09	0.952	12.91	1.513

[a] The two-center energies of the α-C—H and α-C—N bonds.

[b] The order of the α-C—H bond.

[c] The α-C—N bond length.

reagents) in the free electrostatic solvation energy of the TS of reaction (6).

* * *

According to experimental data on the polymerization of allyl acetate in the bulk, the ratio of the preexponential factors of chain propagation and chain transfer reactions is equal to 1.[1] It was shown by the *ab initio* quantum-chemical methods that the entropy factors of the reactions of ethylene dimerization and chain transfer to monomer (abstraction of the hydrogen atom of the CH_2 group by ethyl radical) are equal.[19] This result becomes understandable when it is considered that the TS of two alternative routes of radical reactions are structurally similar; it also suggests that the preexponential factors of chain propagation and chain transfer reactions we have considered are also equal. In this connection it is of interest to consider the differences between the activation energies ($\Delta E_{0,S}$) of competing reaction routes in solution, because the $\Delta E_{0,S}$ values are relative quantities that are independent of temperature corrections (due to the equality of the entropy factors) and solvation effects ΔG_V. Comparison of the $\Delta E_{0,S}$ values for the reactions of radical addition to the double bond and abstraction of the α-hydrogen atom for the three systems studied showed that the activation barriers to chain transfer reactions are higher than the $E_{0,S}$ values for chain propagation reactions, that protonation and quaternization lead to successive decrease in the competing ability of the reaction of chain transfer to monomer, and that this effect increases to a certain extent as the dielectric permittivity of the solvent (ε) decreases (Table 6). According to the experimental data on radical polymerization of allyl acetate in the bulk,[1] the difference in the activation energies of the reactions of abstraction of the mobile hydrogen atom of the allyl group and chain propagation (ΔE_a) is 3 kcal mol^{-1}. A degree of polymerization of about 20 was achieved in this system,[1] whereas even oligomers were not detected in the polymerization of allylamines and diallylamines in the absence of acids or complexing agents.[2–7] Thus, the $\Delta E_{0,S}$ value obtained for the polymerization of compound **1** seems to be rather reasonable.

Table 6. Calculated differences in activation energies of the reactions of addition to the double bond ($E_{0,S}^{(1)}$/kcal mol^{-1}) and those of abstraction reactions of the α-hydrogen atom ($E_{0,S}^{(2)}$/kcal mol^{-1}) and experimentally observed degrees of polymerization (n)

Reactions compared	$\Delta E_{0,S} = E_{0,S}^{(2)} - E_{0,S}^{(1)}$ (calculation)		k_{add}/k_{tr} (estimate)[a]	n (experiment)
	ε = 25	ε = 80		
(1a) and (4)	0.6	0.6	~3	—[b]
(2a) and (5)	1.6	1.2	~8	~7; <100[c]
(3a) and (6)	2.5	2.4	~55	≥100[d]

[a] Estimate obtained using the data for $\Delta E_{0,S}$ (ε = 80, T = 25 °C) listed in this table and taking into account the equality of the preexponential factors.

[b] No polymer was isolated.[2–7,10]

[c] Polymerization of compound **1** in the presence of HCl [8] (at T = 30 °C) and polymerization of allylamine in the presence of excess H_3PO_4 under conditions of photolytic initiation (at T = 20 °C),[4] respectively.

[d] See references cited in Refs. 10 and 11.

On the whole, the ratios of the rate constants for chain propagation and chain transfer reactions assessed from the equality of the preexponential factors are in satisfactory agreement with the experimental data (see Table 6). It is obvious that the $\Delta E_{0,S}/(RT)$ ratio will decrease with increasing temperature, *i.e.*, the competing ability of chain transfer reactions will increase. In fact, the degree of allyl acetate polymerization decreases from 25 to 18 as temperature increases from 60 to 85 °C.[1]

Analysis of the results obtained and the reported data shows that the presence of a sufficient amount of stable protonated forms of the monomer and a minimum amount of nonprotonated forms in the polymerizing system is a necessary condition for the decrease in the competing ability of chain transfer reactions upon polymerization of non-quaternary compounds of the diallylamine series (in particular, amine **1**). The use of quaternary derivatives in the form of salt **4**, first, provides the possibility of existence of stable ionogenic forms of the monomer and propagation radicals and, second, leads, as has been shown above, to an additional increase in the activation energies of chain transfer reactions due to solvation effects.

Obviously, it is difficult to reach an equilibrium at which the base could exist only in its protonated form in the acid—base system and it seems likely this was the case in the polymerization systems studied previously.[3–8] Nevertheless, there is a possibility of reaching such an equilibrium. For instance, it was shown by IR Fourier spectroscopy that in dilute nonpolar solutions of complexes of several pyridines (with $pK_a \geq 6.37$) and trifluoroacetic acid, CF_3COOH, the equilibrium is shifted toward the formation of ionized structures only.[30] Taking into account that the pK_a values for diallylamines are no less than 9, the study of their polymerization in the presence of CF_3COOH seems to be promising.

Thus, we obtained results that are adequate for the experimental data on both qualitative and quantitative levels using semiempirical computational methods with small expenditures of computing time (no longer than 30 min for calculations of TS in vacuum and no longer than 3 h for calculations of electrostatic solvation energies on a Pentium-166 personal computer). In the case of *ab initio* calculations of this type of reactions for a more simple system (ethyl radical—ethylene) without considering solvation effects, good quantitative agreement with experiment was achieved only at high levels

of theory (*e.g.*, QCISD(T)/6-311G** calculations of TS on an IBM RS/6000 workstation take about two weeks),[19,26] whereas the neglect of electron correlation and the use of smaller basis sets leads to a considerable deterioration of results.[19,26] From this point of view the use of semiempirical computational methods with consideration of solvation effects in the studies of reaction mechanisms (and search for transition states) of rather large chemical systems with open electron shells is justified.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-32773a).

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Received June 3, 1998;
in revised form October 26, 1998