Brief Communications

Energy barriers to degenerate rearrangements of long-lived carbocations: quantum chemical calculations *vs*. experiment*

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Density functional calculations of energy barriers to degenerate rearrangements of long-lived carbocations that occur by 1,2-shifts of various atoms and groups were performed. The results obtained were compared with the available experimental data. Good agreement was found for hydrocarbon migrants. Possible reasons of discrepancies in the case of hydrogen migrant and migrants containing heteroatoms are discussed.

Key words: carbocation, degenerate rearrangement, quantum chemical calculations, density functional theory, energy barrier.

Rearrangements of carbocations generated in superacids (so-called long-lived carbocations) have a high synthetic potential. A number of relevant examples are shown in Scheme 1. Such rearrangements result in cations with other cyclic systems, occur at room temperature, and provide a nearly quantitative yield of the products obtained upon neutralization of acid solutions.[1—4] However, at present these reactions are not used for synthetic purposes because of low predictability of their results owing to multistage character and very large number of possible pathways. Each pathway includes a sequence of one-step processes, among which the 1,2-shifts of migrants or σ-bonds to a neighboring carbocationic center play the key role. The possibility for the rearrangements of initial and intermediate carbocations to follow several pathways leads to branched reaction schemes (graphs) containing tens of structures.[5] An ICAR program[6] permits automated construction of such graphs.[7] In order to predict the results of a rearrangement, one should estimate the relative stability of each structure and the activation barriers to corresponding reaction paths. Evaluation based on the available experimental data is only reliable for close analogs. The molecular mechanics and semiempirical quantum chemical methods are almost inapplicable for the activation barrier calculations, while the *ab initio* methods are time-consuming. In this situation good results can be obtained from density functional quantum chemical calculations using recently developed, fast and efficient programs, *e.g.*, the PRIRODA program.[8]

* Dedicated to the memory of Academician V. A. Koptyug on the occasion of the 75th anniversary of his birth.

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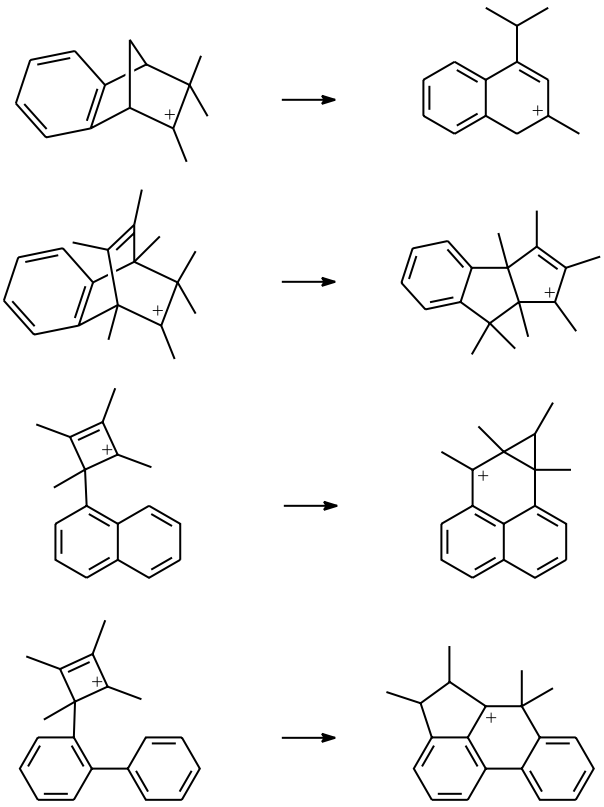
Scheme 1



In order to make the results of rearrangements more predictable and thus reliable, one should determine the applicability range of and typical errors in computational methods. This requires a comparison of the experimental data on the relative stabilities of carbocations and the heights of activation barriers with the results of corresponding calculations using a representative set of compounds. When considering the activation barriers, it is logical to use degenerate rearrangements, because the barriers to such processes are unaffected by the energy difference between the initial and final states. According to Marcus, the kinetic characteristics of the degenerate processes are basic to structural-kinetic theory.[9] To date, numerous experimental data on the rates of degenerate rearrangements of long-lived carbocations occurring by 1,2-shift of various atoms and atomic groups[10] have been accumulated. A number of correlation equations[10—12] for quantitative description of these data were proposed.

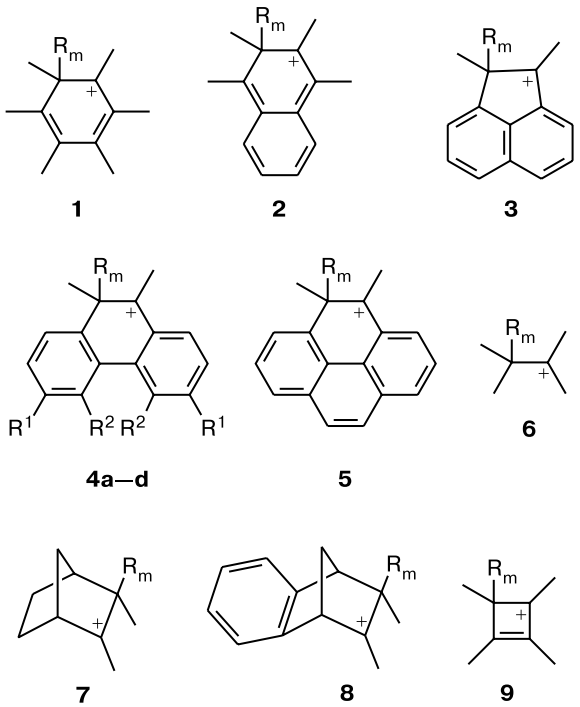
The aim of this work was to study the possibility of prediction of the rates of degenerate carbocation rearrangements based on the results of quantum chemical calculations of the energy barriers to these processes.

Calculation Procedure

Density functional quantum chemical calculations of the geometric and energy characteristics of carbocations were carried out in the PBE approximation[13] using the PRIRODA program[8] (3z basis set, (11s6p2d)/[6s3p2d] contraction pattern for the C, N, O, and F atoms and the (5s1p)/[3s1p] contraction pattern for the H atom) on personal computers with the Athlon® 2600+, Athlon® 2500+, and Athlon® 2000+ CPUs. Ground-state geometry optimization usually took about 2 h. Transition states were located as follows: geometry optimization of a system under study with a "frozen" geometric parameter (usually, the R_m—C—C^+ angle) in order to hold the system in the vicinity of transition state, calculations of the Hessian, transition-state geometry optimization, and again calculations of the Hessian. The energy barriers were calculated without inclusion of zero-point vibrational energies.

Results and Discussion

The barriers to degenerate carbocation rearrangements occurring by 1,2-shift of various types of migrants (R_m) were calculated by the PRIRODA program. The results obtained are listed in Table 1 and shown in Fig. 1 for different types of migrants. For the structures having several conformations due to rotation about single bonds we present the energy differences between the transition state and the ground state of the most stable conformers.



4: $R^1 = R^2 = H$ (**a**); $R^1 = Me$, $R^2 = H$ (**b**); $R^1 = CF_3$, $R^2 = H$ (**c**); $R^1 = H$, $R^2 = Me$ (**d**)

Note. Types of migrants R_m are listed in Table 1.

The best agreement between the experimental and theoretical data was obtained for the migrants that are low sensitive to the effect of specific solvation, namely, the Me group, vinyl groups, and aryl groups containing no

Table 1. Calculated and experimental activation barriers (E_a)

Structure	Migrant R_m	E_a*/kJ mol^{-1}		Reference
		Calculations	Experiment**	
1	H	60.3	49.4	10
	Me	82.1	76.1	10
	Et	72.8	67.0	10
	CH_2Ph	43.1	51.9	10
	Ph	64.9	70.2	10
	p-MeC_6H_4	58.6	67.0	10
	m-$CF_3C_6H_4$	70.3	83.6	10
	Cl	48.6	65.7	10
	Br	30.1	43.1	10
	NO_2	10.5	55.3	10
2	H	68.7	53.6	10
	Me	98.8	94.9	10
3	H	64.1	57.8	10
	Me	83.3	77.3	10
	Et	74.1	68.2	10
	Ph	43.5	47.7	10
	p-MeC_6H_4	34.8	39.4	10
	p-$CF_3C_6H_4$	52.3	71.5	10
	cis-CMe=CHMe	27.6	35.8	14
	Cl	23.9	44.0	10
	Br	10.0	21.4	10
	OMe	24.7	39.3	10
	$HOMe^+$	26.8	>164	15
4a	H	52.3	36.4	10
	Me	56.9	51.1	10
	Et	48.6	42.3	10
	Ph	35.6	37.7	10
	p-MeC_6H_4	26.8	27.2	10
	p-$CF_3C_6H_4$	43.5	49.0	10
	C_6F_5	61.5	>80	10
	p-$MeOC_6H_4$	14.2	27.2	10
	$CH=CH_2$	22.6	24.4	16
	$CMe=CH_2$	38.5	37	17
	cis-CMe=CHMe	18.8	22.0	18
	trans-CMe=CHMe	35.2	39	17
4b	H	55.3	41.0	10
	Me	62.4	56.1	10
	Ph	43.5	44.8	10
	CH_2Ph	27.6	33.1	10
	CH_2Cl	73.7	74.0	10
4c	Ph	28.5	26.8	10
4d	Me	65.3	59.0	19
5	Me	56.5	49.0	10
6	H	21.4	13.0	10
	Me	14.2	15.9	10
7	H	35.2	30.1	10
	Me	38.1	34.8	10
8	Me	67.8	54.4	10
9	$AlCl_3^-$	38.1	84.9	10

* If necessary, the energy barriers were recalculated from kcal mol^{-1} to kJ mol^{-1} using a coefficient of 4.184.
** If no E_a values were available, $\Delta G^{\#}$ were used.

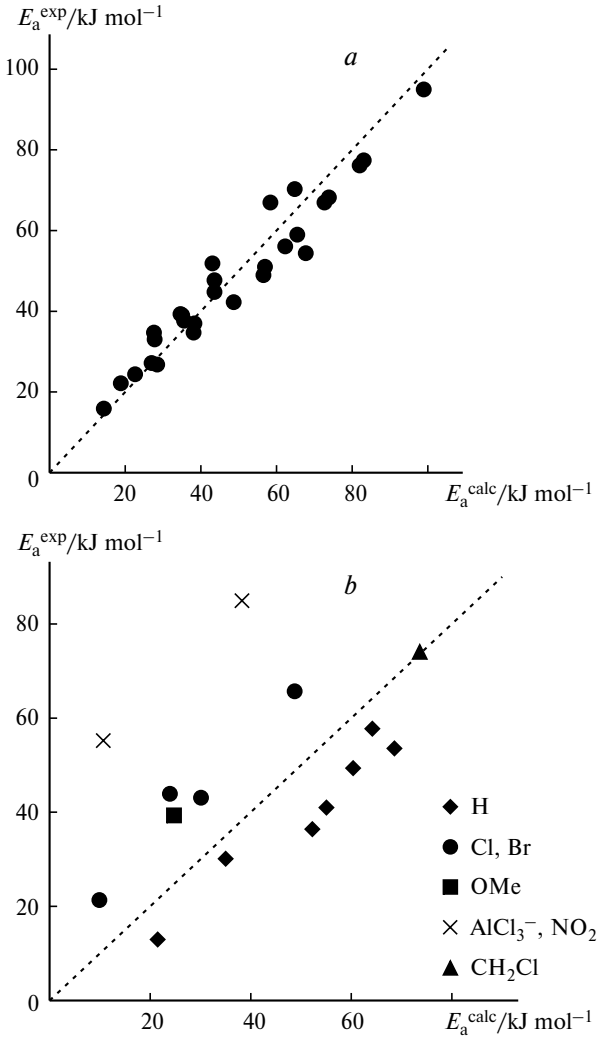


Fig. 1. Calculated and experimental energy barriers (E_a^{calc} and E_a^{exp}, respectively) to rearrangements involving hydrocarbon migrants C_nH_m (*a*) and migrants R_m = H, OMe, Cl, Br, NO_2, $AlCl_3^-$, and CH_2Cl (*b*). Dashed lines are drawn at an angle of 45°.

heteroatoms. The calculated activation energies for the processes involving proton shifts are much overestimated compared to the experimental data. On the contrary, the results of calculations for n-migrants (OMe, Cl, Br) are appreciably underestimated.

It is believed that these discrepancies are due to the medium effects. Namely, in the first case a positive charge appeared on the H atom in the transition state is partially compensated by counterions, while in the second case we deal with predominance of the retardation effect of the acid medium, which is due to the formation of hydrogen bonds with the n-migrants. Probably, the retardation effect also manifests itself, although being somewhat less pronounced, in the case of 1,2-shifts of aryl groups. It is known that aromatic compounds can form π-complexes

with acids.[20] However, it remains unclear why the largest differences between the results of calculations and experimental data were obtained for *p*- and *m*-trifluoromethylphenyl groups. Probably, in this case the CF_3 group is involved in the formation of hydrogen bonds. Dramatic discrepancies between the results of calculations and experimental data were obtained for the $OHMe^+$ and NO_2 groups. The calculated energy barriers to 1,2-shifts of these groups are much lower than those found experimentally. It is also quite unexpected that the calculated energy barriers to 1,2-shifts of the OMe and $HOMe^+$ groups are very similar (24.7 and 26.8 kJ mol^{-1}, respectively).

Thus, density functional quantum chemical calculations allow a reliable prediction of the energy barriers to degenerate carbocation rearrangements, which occur by 1,2-shift of hydrocarbon migrants and simulate skeletal rearrangements of polycyclic hydrocarbon systems (root-mean-square deviation of the calculated barrier heights from the experimental values is 1.3 kJ mol^{-1}). We believe that further studies will make it possible to allow for the effect of the medium on the energy barriers to the rearrangements and thus to elaborate a reliable method for prediction of the rates of the 1,2-shifts of protons and migrants containing heteroatoms.

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