QUANTUM-CHEMICAL INVESTIGATION OF THE ELECTROPHILE AFFINITY OF MOLECULES OF FIVE-MEMBERED HETEROCYCLES WITH ONE HETERO- ATOM AND SOME MODEL SYSTEMS

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Quantum-chemical calculations have been made of the energy characteristics of the molecules of pyrrole, furan, thiophene, and selenophene, the simplest derivatives of N, O, S, and Se with sp^3- and sp^2-hybridized C atoms and heteroatoms, and also of the products of addition of proton and certain other electrophiles to these molecules . The calculations were carried out by HF, B3LYP, and MP2 methods with the 6-31+G(d) basis set with corrections to the energy of zero-point vibrations. It was shown that the values of the affinity of the nitrogen-containing systems towards the electrophile were significantly greater than for their analogs, derivatives of chalcogens, while the relative stability of the onium states of the latter depends both on the hybridization of the heteroatoms, and also on the nature of the electrophile. Analysis of the obtained results made it possible to build a stability series of the onium compounds and to interpret the special features of the positional selectivity in electrophilic substitution reactions of five-membered heteroaromatic compounds with one heteroatom.

It is known that the reactivity (substrate selectivity) of five-membered heterocycles with one heteroatom in electrophilic substitution reactions depends on attack of the electrophile at the most reactive α-position and falls in the series pyrrole >> furan > selenophene > thiophene [1]. It seemed that the positional selectivity (the α:β ratio) must be increased in the same sequence. However the observed change in positional selectivity in the series furan > selenophene > thiophene > pyrrole [1, 2] does not correlate with the substrate selectivity data given above.
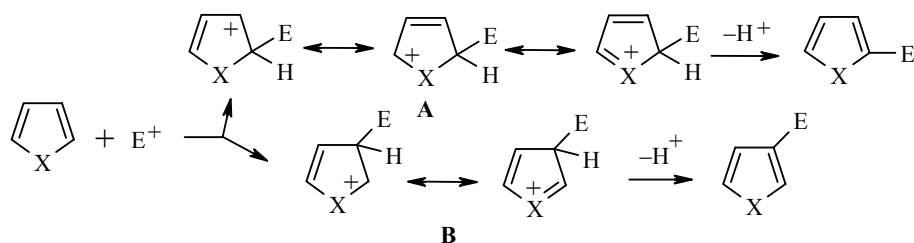
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* Dedicated to the remarkable heterocyclic chemist Aleksandr Fedorovich Pozharskii on his 70th jubilee.
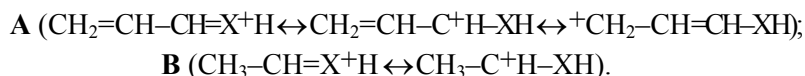
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To explain the reasons for the nonagreement of the indicated series for substrate and positional selectivity a hypothesis was put forward previously by one of us [3, 4], based on an analysis of the features of the structure of cationic σ-complexes which are intermediates in the electrophilic substitution of five-membered heterocycles with one heteroatom (Scheme 1). According to this hypothesis, the formation of β-substituted compounds, proceeding through a σ-complex of type **B**, in which only the heteroatom X and one of the α-carbon atoms participate in the delocalization of charge, must depend more on the ability of the heteroatom X to exist in the onium state, than on the formation of α-substituted compounds, since in the latter case delocalization of charge in a cation of type **A** is effected with the participation of all the atoms of the ring, apart from the geminal C atom. In other words, the sequence given above for the fall in positional selectivity may be caused by the growth in stability of the onium states in the series $O^+ < Se^+ < S^+ < N^+$.

Scheme 1

Such an approach, supplemented by the results of specially carried out quantum-chemical calculations [5, 6], enabled a qualitative interpretation of the available experimental data on the α:β ratios for five-membered heterocycles with one heteroatom as also for the corresponding benzannelated systems. In addition, in a series of cases the problem of constructing reliable sequences of heteroatoms in the indicated series is hindered due to the limitation and ambiguity of information on the relative stability of onium states of atoms of various elements, first of all selenium (from the set considered by us).

In the present work the values calculated by us for the affinity towards proton and other electrophiles of the simple hydrides NH_3, H_2O, H_2S, and H_2Se, their alkyl-substituted derivatives and five-membered heterocycles with one heteroatom are analized. We also analyzed the values of a series of molecules with sp^2-hybridized carbon atoms and heteroatoms, the products of protonation of which may be considered as models of σ-complexes of the following types:

$$A \ (CH_2=CH-CH=X^+H \leftrightarrow CH_2=CH-C^+H-XH \leftrightarrow {}^+CH_2-CH=CH-XH);$$
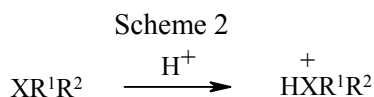$$B \ (CH_3-CH=X^+H \leftrightarrow CH_3-C^+H-XH).$$

Quantum-chemical calculations of the energy characteristics of selected structures are given with full optimization of their geometric parameters by HF, B3LYP, and MP2 methods with the 6-31+G(d) basis set allowing for corrections to the energy of zero-point vibrations with the aid of the Gaussian 98 program set [7].

Values are given in Tables 1-6 of the affinity towards proton (PA) and other electrophiles (EA) for a series of molecules containing a nitrogen atom and chalcogens. The protonation energy taken with the reverse sign (proton affinity), and similar values for other electrophiles, represent the difference of the total energies of the initial molecules and electrophiles and the energies of the addition products. We note that some of the energy characteristics calculated by us and cited further, certainly, were calculated previously by various authors using different quantum-chemical methods or were determined experimentally (see for example, the set of values of basicity and proton affinity in the gas phase, determined for ~1700 molecules, radicals, and atoms [8]). However the incompleteness and ambiguity of the combination of such characteristics necessary for discussing

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obliged us, with the aim of uniformity, to carry out the appropriate quantum-chemical calculations by the methods indicated above. It is also evident that in essence the differences in the basicity of molecules with the different heteroatoms are considered below.

The values given in Table 1 for the proton affinity PA(X) for molecules with sp^3-hydridized heteroatoms X, linked with hydrogen atoms and simple alkyl substituents, when the heteroatoms are protonated (Scheme 2), correspond to the qualitative series of relative stability $N^+ > Se^+ \geq S^+ > O^+$.

<div align="center">

Scheme 2

$$XR^1R^2 \quad \xrightarrow{\ \ H^+\ \ } \quad HXR^1R^2{}^+$$

$X = NH, O, S, Se; R^1 = H, Me, Et, \textit{n}\text{-Pr}; R^2 = H, Me$

</div>

The higher values of PA(N) for molecules containing a nitrogen atom indicate the significant energy preference of proton addition to this atom compared to atoms of oxygen, sulfur, and selenium in the compounds of the type represented in Table 1. For chalcogens the reducing values of PA(X) in the series Se > S > O reflect the fall of energy preference of their protonation in the indicated sequence, while in general PA(Se), PA(S), and PA(O) differ far less from one another than from PA(N).

According to Table 1 the values of PA(X) differ for molecules with the same heteratom X but with different alkyl substituents, and decrease with the reduction of their electron-donating ability. Attention is drawn by the smoothing of differences in relative stability of the onium states of heteroatoms depending on the possible broadening of delocalizing the charge on cations (in this case due to the inductive effect of the substituents), and the accompanying increase in the stability of the proton complexes. The exception is the marked growth in the energy preference of the protonation of dimethyl sulfide and dimethyl selenide over dimethyl ether in comparison with that observed in the series of monomethyl derivatives, which is probably linked with the increased electronegativity of the oxygen atom.

TABLE 1. Values of the Proton Affinity PA(X) (kcal/mol) for Molecules with sp^3-Hybridized Heteroatoms X, Calculated with the 6-31+G(d) Basis Set with Corrections to the Energy of Zero Vibrations and Established Experimentally [12]

Molecule	Method	$R^1 = H$, $R^2 = H$	$R^1 = Me$, $R^2 = H$	$R^1 = Et$, $R^2 = H$	$R^1 = \textit{n}\text{-Pr}$, $R^2 = H$	$R^1 = Me$, $R^2 = Me$
NHR^1R^2	HF	204.1	215.5	218.7	220.0	222.6
	B3LYP	202.0	212.7	216.1	217.4	219.1
	MP2	202.3	212.6	215.3	216.4	219.1
	Exp.	204.0	214.9	218.0	219.4	222.2
SeR^1R^2	HF	168.5	184.4	187.7	188.9	197.3
	B3LYP	171.0	185.9	189.4	190.8	198.0
	MP2	167.3	181.6	184.4	185.4	193.1
	Exp.	—	—	—	—	—
SR^1R^2	HF	164.4	181.1	185.1	186.6	194.2
	B3LYP	165.2	181.1	185.5	187.1	193.6
	MP2	164.7	179.2	182.6	183.9	190.5
	Exp.	168.5	184.8	188.7	190.0	198.6
OR^1R^2	HF	161.9	179.5	184.7	186.2	188.7
	B3LYP	160.4	175.9	182.1	183.6	184.4
	MP2	159.7	175.1	180.0	181.4	183.4
	Exp.	165.2	180.3	185.6	188.0	189.3

Analogous results were obtained on comparing the values of affinity towards methyl cation MeA(X), given in Table 2 for analogous simple molecules with sp^3-hybridized heteroatoms. As on protonation, in all cases the series $N^+ > Se^+ > S^+ > O^+$ was observed while the energy advantage of N over Se was far less (depending on the method, the difference of the values of affinity towards methyl cation of nitrogen-containing and selenium-containing molecules ΔMeA(N–Se) was found within the limits of 9.5 to 22.1 kcal/mol), Se over S was somewhat greater (ΔMeA(Se–S) = 3.6 to 9.5 kcal/mol), and S over O was much greater (ΔMeA(S–O) = 7.3 to 19 kcal/mol) on methylation, than on protonation of the same molecules (ΔPA(N–Se) = 21.1 to 35.6, ΔPA(SE–S) = 1.8 to 5.8, ΔPA(S–O) = 0.4 to 9.2 kcal/mol, Tables 1 and 2). With an increase in the number of electron-donating methyl substituents the differences between MeA(S) and MeA(Se) were smoothed down and

TABLE 2. Values of the Affinity to Methyl Cation MeA(X) (kcal/mol) for Molecules with sp^3-Hybridized Heteroatoms X, Calculated with the 6-31+G(d) Basis Set with Corrections to the Energy of Zero Vibrations

Molecule	Method	$R^1 = H, R^2 = H$	$R^1 = Me, R^2 = H$	$R^1 = Me, R^2 = Me$
NHR^1R^2	HF	87.4	97.8	103.6
	B3LYP	103.4	113.6	119.1
	MP2	105.1	116.7	124.1
SeR^1R^2	HF	65.3	78.2	89.6
	B3LYP	86.5	98.8	109.6
	MP2	85.3	98.4	110.0
SR^1R^2	HF	57.5	72.8	85.1
	B3LYP	77.0	92.0	103.9
	MP2	79.2	94.2	106.4
OR^1R^2	HF	50.2	63.7	70.2
	B3LYP	65.3	78.4	84.9
	MP2	64.6	79.4	87.9

TABLE 3. Values of Affinity to Proton PA(X) (kcal/mol) for Molecules with sp^2-Hybridized Heteroatoms X, Calculated with the 6-31+G(d) Basis Set with Corrections to the Energy of Zero Vibrations, and Established Experimentally [8]

Molecule	Method	R = H	R = Me	R = Et	R = CH$_2$=CH–
RCH=NH	HF	210.6	220.8	222.8	224.7
	B3LYP	204.7	215.9	218.1	220.0
	MP2	203.1	212.5	214.2	215.2
	Exp.	203.8	211.5	–	218.0
RCH=Se	HF	183.4	193.2	195.0	199.5
	B3LYP	183.0	193.6	195.3	198.5
	MP2	176.2	185.0	186.2	189.0
	Exp.	182.6	—	—	—
RCH=S	HF	180.9	191.2	193.6	198.3
	B3LYP	178.8	190.2	192.9	196.2
	MP2	175.0	184.2	186.4	188.8
	Exp.	181.6	—	—	—
RCH=O	HF	170.5	183.0	185.9	191.4
	B3LYP	164.0	179.1	182.4	187.2
	MP2	160.9	173.8	176.7	180.6
	Exp.	170.4	183.7	187.9	190.5

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their values in the series $N^+ > Se^+ > S^+ > O^+$ became closer to MeA(N) and further from MeA(O). The autosuggested hypothesis on the important role of steric interactions on methylation is thereby confirmed. The close disposition of the maximum possible number of methyl groups around the atoms of nitrogen and oxygen is accompanied by lower energy advantages than the formation of cations on adding Me^+ to these atoms in comparison with sulfur and selenium atoms.

In the case of molecules with sp^2-hybridized heteroatoms, according to the data for protonation given in Table 3, the relative stability series $N^+ > Se^+ > S^+ > O^+$ is also observed. Table 3 shows that the values of PA(X) for molecules with one heteroatom X depend markedly on the character of the substituent remote from the cationic center and, as previously (see Table 1), decrease with the reduction in the electron-donating ability of the substituent. The special feature in this case is the significant increase in the energy preference for the protonation of molecules containing sulfur and selenium atoms over the oxygen-containing compounds (depending on the method, for ethyl ΔPA(S–O) = 7.7 to 10.5, ΔPA(Se–O) = 9.1 to 12.9 kcal/mol, for vinyl ΔPA(S–O) = 6.9 to 9.0, ΔPA(Se–O) = 8.1 to 11.3 kcal/mol) in comparison with that which is displayed on protonation of molecules with sp^3-hybridized heteroatoms and the same number of carbon atoms (for ethyl ΔPA(S–O) = 0.4 to 3.4, ΔPA(Se–O) = 3.0 to 7.3 kcal/mol).

In this connection it is interesting to consider, in the example of the simplest molecules with sp^2-hybridized heteroatoms, the possible dependence of the disposition of nitrogen atoms and chalcogens in a series of relative stability of their onium states on the nature of electrophiles, as a result of the addition of which cationic centers are formed. Values are given in Table 4 for the affinity to proton, methyl cation, silyl cation, and borane. On going from protonation to methylation, as for molecules with sp^3-hybridized heteroatoms (Tables 1 and 2), the energy preference of N over Se is strongly reduced, but Se over S and S over O grow (see ΔMeA(N–Se) = 13.4 to 19.3, ΔMeA(Se–S) = 2.5 to 5.7, ΔMeA(S–O) = 14.3 to 21.8 kcal/mol and ΔPA(N–Se) = 21.7 to 27.2, ΔPA(Se–S) = 1.2 to 4.2, ΔPA(S–O) = 10.4 to 14.8 kcal/mol; Table 4). Similar changes also occur on going from protonation to silylation, with the exception that the difference in values of the affinity of S and O for SiH_3^+ is not increased, but is on the other hand strongly reduced and even, according to the data of the HF method (Table 4), becomes negative (-4.0 kcal/mol), i.e. S and O change places in the order. The difference in values of the affinity of N and Se towards BH_3 (10 to 12 kcal/mol) is far less than for three other electrophiles. In the case of Se and S they are approximately the same (1.3 to 3.3 kcal/mol) as on adding proton, but for S and O, although also reduced (0.2 to 6.0 kcal/mol) in comparison with those pertaining to protonation (10.4 to 14.8 kcal/mol), but not so significantly as on silylation (-4.0 to 2.8 kcal/mol; Table 4).

TABLE 4. Values of the Affinity to Electrophiles EA(X) (kcal/mol) for the Simplest Molecules with sp^2-Hybridized Heteroatoms X, Calculated with the 6-31+G(d) Basis Set with Corrections to the Energy of Zero Vibrations

Molecule	Method	Electrophiles			
		H^+	Me^+	SiH_3^+	BH_3
$CH_2=NH$	HF	210.6	95.7	76.2	17.3
	B3LYP	204.7	110.3	76.8	28.3
	MP2	203.1	111.1	78.1	28.7
$CH_2=Se$	HF	183.4	76.4	56.8	5.3
	B3LYP	183.0	96.9	63.2	18.3
	MP2	176.2	94.1	60.0	17.0
$CH_2=S$	HF	180.9	72.2	50.4	2.0
	B3LYP	178.8	91.2	56.3	15.1
	MP2	175.0	91.6	54.8	15.7
$CH_2=O$	HF	170.5	57.9	54.4	1.8
	B3LYP	164.0	71.7	53.5	9.9
	MP2	160.9	69.8	53.4	9.7

The far from exhaustive examples of the simple systems which are given above, show that in spite of the similar sequence of atoms in practically all the cases considered of elements in the relative stability series of their onium states $N^+ > Se^+ > S^+ > O^+$, the values qualitatively characterizing this sequence may be changed widely and in a different way depending on the nature of the initial molecules (as bases) and attacking electrophiles. Allowing for this, and with the aim of developing further the possibility of the model approach selected by us, an attempt was made to approve such structures, which may be considered as "transitional" from the simplest molecules to five-membered heterocycles, comparing values calculated for them with the data for the heterocycles themselves.

The cation $CH_2=CH–CH=X^+H$ is an acyclic comparatively simple model fragment of an σ-complex formed as a result of electrophilic attack by proton at the α-position of a five-membered heterocycle, in which the same delocalization of charge as in a σ-complex is possible. This cation is generated on adding an electrophile to the terminal sp^2-hybridized heteroatom X of the conjugated heterodiene. It is possible to model the β-route of substitution in the heterocycle (see Scheme 1), effecting attack at the β-C atom of the carbon-carbon double bond of ethylene derivatives $CH_2=CH–XH$, in which the vinyl fragment is linked with an sp^3-hybridized heteroatom.

Values are given in Table 5 for the proton affinity of the corresponding heterodienes and ethylenes. For the heterodienes protonated at the heteroatom this value corresponds to the relative stability series $N^+ > Se^+ > S^+ > O^+$ while the difference $\Delta PA(X)$ for it is exactly the same as for the series of analogous protonated molecules with one double bond C=X (see PA(X) in Table 5 for heterodienes and in Table 3 for R = Et), but somewhat smoothed, which is explained by the development in heterodienes of the possibilities of delocalizing the charge due to conjugation.

TABLE 5. Values of the Proton Affinity PA (kcal/mol) Calculated with the 6-31+G(d) Basis Set with Correction to the Energy of Zero Vibrations and Determined Experimentally [8] for Molecules with Heteroatoms X, Modeling Fragments of Five-membered Heterocycles*

Molecule	Method	PA(X)	Molecule	Method	PA(β-C)
$CH_2=CHCH=NH$	HF	224.7	$CH_2=CH–NH_2$	HF	226.6
	B3LYP	220.0		B3LYP	220.3
	MP2	215.2		MP2	218.3
	Exp.	218.2		Exp.	215.0
$CH_2=CHCH=Se$	HF	199.5	$CH_2=CH–SeH$	HF	195.0
	B3LYP	198.5		B3LYP	196.7
	MP2	189.0		MP2	190.6
	Exp.	—		Exp.	—
$CH_2=CHCH=S$	HF	198.3	$CH_2=CH–SH$	HF	194.7
	B3LYP	196.2		B3LYP	194.7
	MP2	188.8		MP2	190.9
	Exp.	—		Exp.	—
$CH_2=CHCH=O$	HF	191.4	$CH_2=CH–OH$	HF	199.7
	B3LYP	187.2		B3LYP	193.9
	MP2	180.6		MP2	189.6
	Exp.	199.5		Exp.	—

* Hydrogen atoms at the heteroatom X and the α-carbon atom in the initial molecules and the products of protonation, where isomers are possible are found in the *anti* position. In molecules of $CH_2=CH–XH$ the β-carbon atom is subjected to protonation.

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It is impossible to show analogs for ethylenes among the model structures used above, since cations of CH_2=CHX are formed as a result of attack not at heteroatoms but at the β-carbon atoms. In spite of the fact that the same products arise on such protonation, which are considered for simple molecules with sp^2-hybridized heteroatoms (Table 3, R = Me), only the absolute energy preference of the onium state of N^+ over Se^+, S^+, and O^+ remains. For the chalcogens, the predicted series becomes ambiguous even qualitatively (depending on the method of calculation).

Values are given in Table 6 of the proton affinity at α- and β-protonation of unsubstituted five-membered aromatic heterocycles. We note that the experimental data given in Table 6 were assigned by us to the significantly more advantageous α-protonation, although the values obtained experimentally certainly include an insignificant contribution of β-protonation as well (concerning the ratio of products of attack of electrophiles at the α- and β-positions of five-membered heterocycles see [1]). From a comparison of Tables 5 and 6 it is possible to discover that some features of the differences in relative stability of nitrogen, selenium, sulfur, and oxygen atoms (ΔPA), revealed in the example of protonation of vinyl derivatives CH_2=CH–XH, when the onium centers are formed not on direct attack of heteroatoms, are displayed to a greater extent in the series of these heterocycles, than are detected for acyclic model systems CH_2=CH–CH–X. Qualitatively (according to results of calculations by the B3LYP and MP2 methods) for α- and β-isomers of σ-complexes, the series of relative stability have the previous form $N^+ > Se^+ > S^+ > O^+$ (see Table 6). However on α-attack by proton the difference in PA for heteroaromatic compounds of nitrogen and selenium, and also of sulfur and oxygen are significantly less than for the inherent heterodienes (see ΔPA(N–Se) = 21.5 to 26.2, ΔPA (Se–S) = 0.2 to 2.3, ΔPA(S–O) = 6.9 to 9.0 kcal/mol (Table 5) for heterodienes and ΔPA(N–Se) = 8.9 to 15.6, ΔPA(Se–S) = 1.8 to 3.3, ΔPA(S–O) = -4.6 to 1.1 kcal/mol (Table 6) for α-protonation). On β-attack by proton the nitrogen-containing and selenium-containing heterocycles are also close to one another in ΔPA(β–C), but their S and O analogs differ more widely (methods B3LYP and MP2) than the corresponding derivatives of ethylene (see ΔPA(N–Se) = 23.6 to 27.7, ΔPA(Se–S) = -0.3 to 2.0, ΔPA(S–O) = 0.8 to 1.3 kcal/mol (Table 5) for ethylenes and ΔPA(N–Se) = 14.2 to 15.7, ΔPA(Se–S) = 1.1 to 2.4, ΔPA(S–O) = 3.3 to 4.5 kcal/mol (Table 6) for β-protonation).

TABLE 6. Values of Proton Affinity PA (kcal/mol) for Five-membered Aromatic Heterocycles Calculated with the 6-31+G(d) Basis Set with Corrections to the Energy of Zero Vibrations and Established Experimentally [8]

Molecule	Method	PA(α-C)	PA(β-C)
(N, H)	HF	216.3	209.3
	B3LYP	208.8	203.2
	MP2	201.4	197.1
	Exp.	209.4	—
(Se)	HF	200.7	188.8
	B3LYP	199.9	189.0
	MP2	189.7	181.4
	Exp.	—	—
(S)	HF	198.7	187.5
	B3LYP	196.6	186.6
	MP2	187.9	180.3
	Exp.	189.1	—
(O)	HF	203.3	189.6
	B3LYP	195.5	183.3
	MP2	187.1	175.8
	Exp.	192.2	—

The results of quantum-chemical calculations of the energy characteristics of heteroaromatic compounds with heteroatoms N, O, S, and Se, their simple derivatives, and addition products with a series of electrophiles, indicate that the electrophilic affinity for nitrogen-containing molecules is greater than for the corresponding O, S, and Se analogs. The differences in relative stability of the onium states of the heteroatoms depend significantly on their hybridization and are smoothed depending on the extending of the possibilities of delocalization of the charge in the resulting cations. The use of adequate structures of small size enables simplification of the creation of stability series of onium states of heteroatoms in heterocyclic compounds and of the interpretation of the features of their positional selectivity in electrophilic substitution reactions.

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