The energetics of resonant dissociative electron attachment to molecules of five-membered heterocyclic compounds

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The thermochemistry of resonant dissociative electron attachment processes for furan, thiophene, selenophene, and pyrrole molecules has been studied. The structures of the dissociation products originating from negative molecular ions at energies ranging from 2 to 6 eV have been established using the measured appearance energies of fragment ions and the known thermodynamic functions of radical and molecular dissociation products. Heats of formation and electron affinities for some radicals and molecules have been assessed by calculations and estimated experimentally. It has been concluded that the majority of the fragment ions are formed *via* rearrangement processes in molecular or fragment ions.

Key words: resonant dissociative attachment; five-membered heteroaromatic compounds.

Although thermochemical methods are widely and successfully used in electron impact mass-spectrometry for studying positive ions, they were very rarely applied to investigate negative ions (NI), especially those of polyatomic organic molecules. The main reason is the lack (or low accuracy) of the constants necessary for thermochemical calculations, namely, the enthalpies of formation ($\Delta H^0{}_f$) of NI and the electron affinities (E_{ea}) of molecules and free radicals. Moreover, if the negative ions are formed by resonant dissociative electron attachment (RDEA), one must take into account the excess energy E^* which may be quite large. At the same time, the thermochemical approach seems very promising in this respect since it can provide information on the structures of ions and coincidently formed neutral species (molecules and radicals).

In this paper we consider the thermochemistry of RDEA processes for some five-membered heterocyclic molecules, namely, furan (**1**), thiophene (**2**), selenophene (**3**), pyrrole (**4**), *N*-methylpyrrole (**5**), and 2,5-dimethylpyrrole (**6**). The furan molecule was studied by us previously,[1] but here more accurate data are presented.

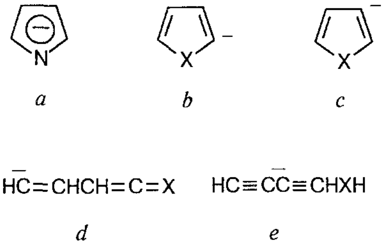
From the experimentally measured values of the appearance energy (E_{ap}) of the fragment ions (A^-), formed in the reaction $AB + \bar{e} \rightarrow AB^{*-\cdot} \rightarrow A^- + B^\cdot$, the thermodynamic functions $\Delta H^0{}_f(A^-)$ and $\Delta H^0{}_f(B^\cdot)$ were calculated with the help of equation

$$E_{ap}(A^-) = \Delta H^0{}_f(A^-) + \Delta H^0{}_f(B^\cdot) - \Delta H^0{}_f(AB) + E^*,$$

where the excess energy E^* is the sum of E_v and E_t, the internal vibrational and kinetic energies of the fragments, respectively. For some processes the E_t values were obtained from the halfwidth at half-maximum (d, m/z) of the corresponding metastable peaks at the accelerating voltage U/B using the formula $E_t = d^2M^2U/16m_1{}^3m_2$,[2] where M, m_1, and m_2 are the mass numbers of the decaying and fragment ions and the neutral product, respectively. E^* was determined as the difference between the experimental value E_{ap} and $E_{ap}{}^{cal}$ calculated from the energy balance of the reaction. In order to establish the most probable structures of the dissociation products formed by the negative molecular ion (NMI) $M^{-\cdot}$, we used the rules according to which the excess energy E^* of the negative ion should be minimal.[3]

The appearance energies of the fragment ions formed by the molecules **1**—**6** are presented in Table 1, which shows that the RDEA processes occur in several energy domains. The attachment of an electron to the pyrrole molecule in the low energy region (E_{ap} = 1.95 eV) leads to splitting of the hydrogen atom and the formation of a stable pyrrolyl-anion (Scheme 1, *a*). An analogous process yielding cyclopentadienyl-anion with E_{ap} = 1.7 eV was observed in the resonant dissociative attachment of an electron to cyclopentadiene.[4] The $\Delta H^0{}_f$ value for ion *a* determined from the measured E_{ap} is

Scheme 1



$\overline{HC}{=}CHCH{=}C{=}X$ *d*

$HC{\equiv}\overline{CC}{\equiv}CHXH$ *e*

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78.7 kJ mol^{-1}. From this figure and E_{ea}($C_4H_4N^{\cdot}$) ~2.39 eV[5] the heat of formation was found to be equal to 309.4 kJ mol^{-1}.

Ion *a* is not formed in the resonant dissociative attachment of an electron to *N*-methylpyrrole **5** in the ~2 eV energy range.

The appearance of $(M-Me)^-$ ions from compound **6** and $(M-H)^-$ ions from **1**—**3** in the same energy range 2.95—3.15 eV (Table 1) reveals the similarity in their structures (*b*). The $\Delta H^0{}_f$ values calculated from the corresponding E_{ap} for ions *b* are 51.1 (X = O), 196.8 (X = S), and 245.8 kJ mol^{-1} (X = Se). $(M-H)^-$ ions of structure *c* do not appear for this resonant state. It was impossible to identify ions *b* as the dissociation products of pyrrole NMI in the 3 eV energy range due to the superimposition of the intense process yielding ions *a* from a close-lying resonance state. However, they can be seen in the mass-spectrum of molecule **5** where peaks corresponding to $(M-H)^-$ ions with E_{ap} = 3.5 eV were observed. In the same energy domain the rearranged $NC_2H_2^-$ ions were found with E_{ap} = 3.3 eV:

$$[\mathrm{HNC_4H_4}]^- \longrightarrow \bar{\mathrm{C}}\mathrm{H_2C{\equiv}N} + \mathrm{H\dot{C}{=}CH_2} \ (E_{ap}{}^{cal} = 2.9 \text{ eV})$$

E_{ap} values calculated for the processes

$$[\mathrm{SC_4H_4}]^- \longrightarrow \mathrm{S}^{-\cdot} + \mathrm{H_2C{=}C{=}C{=}CH_2} \ (E_{ap}{}^{cal} = 3.15 \text{ eV})$$

$$[\mathrm{SeC_4H_4}]^- \longrightarrow \mathrm{Se}^{-\cdot} + \mathrm{H_2C{=}C{=}C{=}CH_2} \ (E_{ap}{}^{cal} = 2.2 \text{ eV})$$

are in good agreement with E_{ap} of $S^{-\cdot}$ (3.1 eV) and $Se^{-\cdot}$ (3.0 eV) ions determined experimentally from the mass spectra of molecules **2** and **3**. If the neutral fragments have the $HCCCH{=}CH_2$ structure, then the appearance energies of $S^{-\cdot}$ and $Se^{-\cdot}$ should be equal to 2.6 and 1.65 eV, respectively. Indeed, these ions were identified with E_{ap} = 1.5 and 1.3 eV. However, experiments with a false cathode revealed that the source of the $S^{-\cdot}$ ions is the decomposition of thiophene on the cathode rather than the resonant process.[6] The very low appearance energies of SH^- and SeH^- ions (1.8 and 1.4 eV, respectively) are also inconsistent, since even if the neutral species $HCCC^{\cdot}{=}CH_2$ with the lowest possible $\Delta H^0{}_f$ = 515.0 kJ mol^{-1} ($HCCC^{\cdot}{=}CH_2$) are formed coincidently, E_{ap} of these ions should be equal to 3.3 and 2.7 eV, respectively. The SH^- and SeH^- ions with such low E_{ap} may be formed in chemical reactions on the surface of the ionization chamber. Other examples of the appearance of such "spurious" ions are known,[7] but have not yet been studied in detail.

The $(M-H)^-$ ions in the energy range ~5—6 eV are due to the splitting the α- or β-hydrogen atom from NMI **1**—**4** (for compound **4** cleavage of the imine hydrogen atom also takes place), which preserves the cyclic structure of the ions. Their excess energies exceed the E_{ea} of the corresponding radicals *a*, *b*, and *c* since electron autodetachment processes are observed. On the other hand, $(M-H)^-$ ions possessing excess energy decay to form the fragment ions SeH^-, SC_2H^-, SeC_2H^-, OC_2H^-, $C_3H_3^-$, and SH^-, as follows from the observation of metastable peaks in the mass spectra of the compounds **1**—**3**. It is likely that the $(M-H)^-$ products identified in the 5—6 eV energy domain correspond to a mixture of ions with different structures and the main contribution to the ionic current comes from those with higher enthalpies of formation. These ions may have a linear structure (*d*) with the calculated enthalpies $\Delta H^0{}_f$ = 322.4 (X = Se), 407.4 (X = S), and 352.5 kJ mol^{-1} (X = NH). For ion *d* (X = O) $\Delta H^0{}_f$ = 67.4 kJ mol^{-1} is too small, so it is not likely to be stable with respect to dissociation or electron detachment. The measured value E_{ap} = 5.5 eV for $(M-H)^-$ ions is more consistent with the linear structure $\mathrm{HCCCH{=}\bar{C}{-}OH}$ with $\Delta H^0{}_f$ = 288.1 kJ mol^{-1}, although ions of structure *e* with $\Delta H^0{}_f$ = 159.1 kJ mol^{-1} may contribute a little as well. For the $(M-H)^-$ ions formed from compound **2** structure *e* with $\Delta H^0{}_f$ = 375.1 kJ mol^{-1} is more probable than *d*.

As is evident from Table 1, deep fragmentation of NMI **1**—**3** (in contrast to NMI **4**) takes place in the energy region under study, yielding XC_2H^-, $X^{-\cdot}$, C_4H^-, $C_3H_3^-$, C_2H^-, and XH^- ions. The corresponding appearance energies of the XC_2H^- ions and the existence of metastable peaks in the mass spectra reveal the consecutive decomposition of NMI of these compounds:

$$\mathrm{OC_4H_4}^{-\cdot} \xrightarrow{-\mathrm{H}} \mathrm{OC_4H^-_3} \xrightarrow{*} \bar{\mathrm{O}}\mathrm{C{\equiv}CH} + \mathrm{HC{\equiv}CH}$$
($E_{ap}{}^{cal}$ = 4.9 eV),

$$\mathrm{SC_4H_4}^{-\cdot} \xrightarrow{-\mathrm{H}} \mathrm{SC_4H^-_3} \xrightarrow{*} \bar{\mathrm{S}}\mathrm{C{\equiv}CH} + \mathrm{HC{\equiv}CH}$$
($E_{ap}{}^{cal}$ = 5.0 eV),

$$\mathrm{SeC_4H_4}^{-\cdot} \xrightarrow{-\mathrm{H}} \mathrm{SeC_4H^-_3} \xrightarrow{*} \overline{\mathrm{Se}}\mathrm{C{\equiv}CH} + \mathrm{HC{\equiv}CH}$$
($E_{ap}{}^{cal}$ = 4.8 eV).

The amounts of kinetic energy released in the $OC_4H_3^-$ → OC_2H^- and $SC_4H_3^-$ → SC_2H^- processes calculated from the metastable peaks are 0.39 and 0.32 eV, respectively. Using Franklin's formula[8] $E_t = E^*/\alpha N$ (where N is the number of vibrational degrees of freedom of a metastable ion, in our case $N = 8 \cdot 3 - 6 = 18$), one may estimate the empirical parameter α, whose value reflects the fraction of active vibrational modes, as 0.085 and 0.075 for the above two processes, respectively. The fact that these values are of the same order of magnitude implicitly supports the scheme suggested for the formation of XC_2H^- ions and their tentative structure. To be correct, it should be pointed out that since the energy E_t released upon the formation of intermediate $(M-H)^-$ ions is unknown, the energies E^* were taken as the

Table 1. Appearance energies of negative ions in the mass spectra of compounds **1**—**6**, eV

Compound	Ions							
	$(M-H)^-$	$(M-Me)^-$	C_4H^-	$C_3H_3^-$	C_2H^-	XC_2H^-	XH^-	$X^{-\cdot}$
1	3.15 5.5		5.6	5.5	5.6	5.5	5.5	
2	3.1 5.1		5.85	5.6	5.4	5.45	1.8 5.5	1.5 3.1 5.1 6.0
3	3.0 4.7		4.7		5.0	4.9	1.4 5.2	1.3 3.0 4.9
4	1.95 4.75 5.5					3.3 5.8		
5	3.5 5.4	5.4						
6	4.9	2.95 4.9					5.05	5.0

differences between E_{ap}^{cal} and E_{ap}. The energy release E_t for the $SeC_4H_3^-$ SeC_2H^- process cannot be calculated due to the low intensity of the corresponding metastable peaks in the mass spectrum of compound **3**. Investigating RDEA processes for 2,5-deuterothiophene, Khvostenko *et al.*[9] detected the formation of the SC_2D^- ion and postulated its structure as $^-$SCDC:. However, this ion can result from the migration of a D atom and its structure is likely to be $^-$SCCD as described above. It seems doubtful that the fragmentation of NMI **1**—**3** should give $^-$XCHC: ions (X = O, S, Se) because this process involves the formation of $CH_2{=}CH^{\cdot}$ radicals as neutral fragments; the E_{ea} of $^-$XCHC: (X = O, S, Se) should be 1.5, 2.2, and 2.6 eV, respectively.

The appearance of $NC_2H_2^-$ ions at the measured energy E_{ap} = 5.85 eV in the mass spectrum of molecule **4** corresponds to the processes

$$\mathrm{HNC_4H_4^{-\cdot}} \xrightarrow{-\mathrm{H}} \mathrm{NC_4H^-_4} \xrightarrow{*} \mathrm{\bar{C}H_2N{\equiv}C{:}} + \mathrm{HC{\equiv}CH}$$

(E_{ap}^{cal} = 5.9 eV),

$$\mathrm{HNC_4H_4^{-\cdot}} \xrightarrow{-\mathrm{H}} \mathrm{HNC_4H_3^-} \xrightarrow{*} \mathrm{\bar{N}HC{\equiv}CH} + \mathrm{HC{\equiv}CH}$$

(E_{ap}^{cal} = 5.7 eV).

This resonance may also involve $NC_2H_2^-$ ions of a different structure formed according to the scheme

$$\mathrm{HNC_4H_4^{-\cdot}} \xrightarrow{-\mathrm{H}} \mathrm{HNC_4H_4^-} \xrightarrow{*} \mathrm{N{\equiv}C{-}\bar{C}H_2} + \mathrm{HC{\equiv}CH}$$

(E_{ap}^{cal} = 4.5 eV).

If this process really takes place, its excess energy should be 1.35 eV, a value which is close to those pertinent to the analogous processes for compound **1**. On the other hand, this reaction may result from a resonance of lower energy, where the (M—H)$^-$ ions correspond to the experimental value E_{ap} = 4.75 eV. However, these were not detected. The absence of metastable peaks in the mass spectrum of compound **4** in the chosen energy range (*i.e.*, the lack of data for calculating E_t) prevents one from knowing exactly whether this process actually occurs.

The corresponding metastable peaks in the mass spectra of **1** and **2** indicate that the NMI of these compounds undergo consecutive decomposition yielding $C_3H_3^-$ ions with two possible structures, $HC{\equiv}\bar{C}H_2^-$ and MeC≡C:

$$\mathrm{OC_4H_4^{-\cdot}} \xrightarrow{-\mathrm{H}} \mathrm{OC_4H_3^-} \xrightarrow{*} \mathrm{MeC{\equiv}\bar{C}} + \mathrm{CO}$$

(E_{ap}^{cal} = 3.4 eV), (1)

$$\mathrm{SC_4H_4^{-\cdot}} \xrightarrow{-\mathrm{H}} \mathrm{SC_4H_3^-} \xrightarrow{*} \mathrm{MeC{\equiv}\bar{C}} + \mathrm{CS}$$

(E_{ap}^{cal} = 4.5 эВ), (2)

$$\mathrm{OC_4H_4^{-\cdot}} \xrightarrow{-\mathrm{H}} \mathrm{OC_4H_3^-} \xrightarrow{*} \mathrm{HC{\equiv}C\bar{C}H_2} + \mathrm{CO}$$

(E_{ap}^{cal} = 4.1 эВ), (3)

$$\mathrm{SC_4H_4^{-\cdot}} \xrightarrow{-\mathrm{H}} \mathrm{SC_4H_3^-} \xrightarrow{*} \mathrm{HC{\equiv}C\bar{C}H_2} + \mathrm{CS}$$

(E_{ap}^{cal} = 5.2 эВ), (4)

The excess energies for processes (1) and (2) are 2.1 and 1.1 eV and the E_t values are 0.61 and 0.15 eV, respectively. Franklin's formula[8] estimates the a parameters at 0.191 for furan and 0.401 for thiophene. It is unlikely that this parameter would differ so strongly for similar processes. Moreover, the proposed structure MeC^-C cannot explain the absence of $C_3H_3^-$ ions in the mass spectrum of compound **3** in the same resonance state, because in the latter case $E_{ap}^{cal}(C_3H_3^-)$

must be equal to 4.7 eV. For processes (3) and (4) E^* are 1.4 and 0.4 eV, and the a values were found to be 0.128 and 0.148, respectively. The above arguments enable one to give the preference to the HCC^-CH_2 structure. The $E_{ap}{}^{cal}$ value calculated for the process

$$SC_4H_4{}^{-\cdot} \xrightarrow{-H} SeC_4H_3{}^- \xrightarrow{*} HC{\equiv}C\bar{C}H_2 + CSe$$

is equal 5.45 eV. However, this calculation did not take into account the excess energy which, as follows from the analysis of furan and thiophene fragmentation, is relatively high. It is likely that the resonance state energy of selenophene NMI is too low to produce the HCC^-CH_2 ions. The relatively low appearance energies for the other ions in this case also support this conclusion (see Table 1).

Starting from the measured value of E_{ap} of C_2H^- ions and guessing the different structures for the neutrals which may be formed simultaneously with the HCC^- ion, we picked out the two most probable processes,

$$XC_4H_4{}^{-\cdot} \longrightarrow HC{\equiv}C^- + HC{\equiv}CX^{\cdot} + H_2$$

$E_{ap}{}^{cal}$ = 4.9 (X = O), 5.1 (X = S), and 4.7 eV (X = Se),

$$XC_4H_4{}^{-\cdot} \longrightarrow HC{\equiv}C^- + HC{=}CH + HX^{\cdot}$$

$E_{ap}{}^{cal}$ = 5.4 (X = O), 4.9 (X = S), and 4.2 eV (X = Se).

The structures of the neutral particles were derived from the smallest excess energies of RDEA assuming that these neutral fragments are the same for compounds **1**—**3**.

The C_4H^- ions have the stable structure $HC{\equiv}CC{\equiv}C^-$ (in contrast to other possible structures, for instance, $C{:}{=}CHC{\equiv}C^-$). Sorting the parent neutral fragments reveals the possibility of two processes, namely,

$$XC_4H_4{}^{-\cdot} \longrightarrow HC{\equiv}CC{\equiv}C^- + H_2 + HX^{\cdot}$$

$E_{ap}{}^{cal}$ = 5.1 (X = O), 4.7 (X = S), and 4.0 eV (X = Se);

$$XC_4H_4{}^{-\cdot} \longrightarrow HC{\equiv}CC{\equiv}C^- + H_2X + H^{\cdot}$$

$E_{ap}{}^{cal}$ = 4.5 (X = O), 5.2 (X = S), and 5.1 eV (X = Se).

However, the value $E_{ap}{}^{cal}(C_4H^-)$ for the second process when X = Se exceeds the experimental value by 0.4 eV. Therefore, the reaction yielding C_4H^- ions may follow the first scheme.

The formation of HX^- (X = O, S, Se) ions from compounds **1**—**3** can be accompanied by the production of neutral fragments of various structures (($CH_2{=}CHC{\equiv}C^{\cdot}$, $CH_2{=}{}^{\cdot}CC{\equiv}CH$, ${}^{\cdot}CH{=}CHC{\equiv}CH$, and so on) and the corresponding $E_{ap}{}^{cal}$ values for the HX^- ions are lower than the measured E_{ap}. The metastable peaks in the mass spectra of compounds **2** and **3** also point out the possibility of the process

$$XC_4H_4{}^{-\cdot} \xrightarrow{-H} XC_4H_3{}^- \xrightarrow[*]{} XH^- + HC{\equiv}CC{\equiv}CH$$

$E_{ap}{}^{cal}$ = 5.1 (X = S), 4.5 eV (X = Se).

For X = S the value of E_t is 0.07 eV. The very weak intensity of the metastable peak corresponding to the reaction $SeC_4H_3{}^- \rightarrow SeH^-$makes it impossible to evaluate E_t. In the mass spectrum of **1** the analogous peak does not appear at all, since in this case the value $E_{ap}{}^{cal}(OH^-)$ = 6.1 eV exceeds the measured value by 0.6 eV. Therefore, the OH^- ions may originate only from the molecular ions. Another difference between the NMI **1** fragmentation process and those of compounds **2** and **3** is the absence of $O^{-\cdot}$ ions. The most probable source of $S^{-\cdot}$ and $Se^{-\cdot}$ ions is the reaction

$$XC_4H_4{}^{-\cdot} \longrightarrow X^{-\cdot} + H\dot{C}{\equiv}CC{\equiv}\dot{C}H$$

$E_{ap}{}^{cal}$ = 5.8 (X = S), 4.8 eV (X = Se).

For molecule **2**, however, there is another decay channel for NMI within this energy range which leads to $S^{-\cdot}$ ions and $HC{\equiv}CC{\equiv}CH$ + H_2 neutral fragments ($E_{ap}{}^{cal}$ = 4.5 eV).

Experimental

The mass spectra of negative ions in the resonant electron attachment regime were recorded using a modified MI-1201 mass-spectrometer under the following conditions: accelerating voltage 3.6 kV, electron current ~1 μA, electron distribution at half-maximum $E_{1/2}$ = 0.3 eV, electron energy from 0 to 14 eV. To avoid the temperature effects the ionization chamber was not heated. The electron energy scale was calibrated by the appearance energies of $SF_6{}^-/SF_6$ (~ 0 eV) and $C_6H_5{}^-/C_6H_6$ (~7.8 eV) ions. The following values of $\Delta H^0{}_f$ (kJ mol^{-1}) were used for the molecules and radicals in the paper:[10—13] furan (−34.8), thiophene (115.6), pyrrole (108.4), $^{\cdot}H$ (218.1), S (277.2), Se (235.7), CO (−110.5), CS (142.4), OSe (226.1), $^{\cdot}OH$ (39.4), $^{\cdot}SH$ (144.4), $^{\cdot}SeH$ (135.2), H_2S (−20.1), H_2O (_−241.0), H_2Se (26.8), $HC{\equiv}C^{\cdot}$ (504.5), $MeC{\equiv}C^{\cdot}$ (456.4), $HC{\equiv}CH$ (226.9), $^{\cdot}OC{\equiv}CH$ (216.9), $^{\cdot}SC{\equiv}CH$ (389.4), $CH_2{=}C{:}$ (397.7), $CH_2{=}{}^{\cdot}CH$ (295.2), $CH_2{=}CH_2$ (52.3), $^{\cdot}NHC{\equiv}CH$ (376.8), $^{\cdot}CH_2C{\equiv}CH$ (340.8), $^{\cdot}CH_2N{=}C{:}$ (334.9), $^{\cdot}CH_2C{\equiv}N$ (224.9), $HOCH{=}CH_2$ (−127.3), $HSCH{=}CH_2$ (87.9), $^{\cdot}OCH{\equiv}CH_2$ (12.6), $HOCH{=}C{:}$ (205.2), $HSCH{=}C{:}$ (433.3), $MeCH{=}CH_2$ (−8.8), PhSPh (231.5), PhSePh (290.1), $CH_2{=}C{=}C{=}CH_2$ (342.1), $HC{\equiv}CC{\equiv}C^{\cdot}$ (714.1), $PhCH_2{}^{\cdot}$ (194.7), $CH_2{\equiv}CHC{\equiv}C^{\cdot}$ (556.8), $HC{\equiv}CCH{=}CH_2$ (291.4), $HC{\equiv}CCH{\equiv}CH^{\cdot}$ (527.5), $HC{\equiv}CC{\equiv}CH$ (473.1). The values accepted for R—H bond dissociation energies (BDE, kJ mol^{-1}) were:[10] PhO—H (362.2), PhS—H (341.2), $PhCH_2$—H (362.6), HO—H (499.5), HS—H (382.7), HSe—H (326.6).

The E_{ea} values (eV) for radicals were taken from previous publications:[5,10] $PhCH_2^{\cdot}$ (0.86), S (2.0771), Se (2.0206), $OH^{\cdot}$ (1.82767), $SH^{\cdot}$ (2.317), $SH^{\cdot}$ (2.21), $HC{\equiv}C^{\cdot}$ (2.94), $OC^{\cdot}{\equiv}CH$ (2.35), $PhO^{\cdot}$ (2.36), $PhS^{\cdot}$ (2.47), $PhNH^{\cdot}$ (1.7), $OCH{\cdot}{\equiv}CH_2$ (1.817), $^{\cdot}CH_2N{=}C{:}$ (1.059), ${\cdot}CH_2C{\equiv}N$ (1.543), $CH_2{=}CH^{\cdot}$ (1.5), $^{\cdot}CH_2C{\equiv}CH$ (0.893).

The $\Delta H^0{}_f$ values (kJ mol^{-1}) were calculated or estimated here for the radicals $OCH^{\cdot}{\equiv}C{:}$ (345.1), $^{\cdot}SCH{=}C{:}$ (553.6), $^{\cdot}SeCH{=}C{:}$ (596.9), $^{\cdot}SCH{=}CH_2$ (208.2), $^{\cdot}SeCH{=}CH_2$ (251.5), $HSeCH{=}C{:}$ (486.1), $^{\cdot}SeC{\equiv}CH$ (427.7), $HC{\cdot}{=}CHCH{=}C{=}X$ (467.2 (X = S), 212.2 (X = O), 552.2 (X = Se), 497.3 (X = NH)), $HC{\equiv}CCH{=}^{\cdot}COH$ (317.1), $HC{\equiv}CC{\cdot}{=}CHSH$ (558.5), $HC{\equiv}CC^{\cdot}{=}CHOH$ (342.5), $HC^{\cdot}{=}CHCH{\equiv}{\cdot}CH$ (594.9), and the selenophene molecule (174.2), together with E_{ea} (eV) for the radicals $^{\cdot}SC{\equiv}CH$ (2.46), $^{\cdot}SeC{\equiv}CH$ (2.4), $HC^{\cdot}{=}CHCH{=}C{=}X$ (≡ 1.5 X = O, S, Se, NH), $HC{\equiv}CC^{\cdot}{=}CHXH$ (1.9 X = O, S), $HC{\equiv}CCH{=}^{\cdot}COH$ (0.3), $^{\cdot}NHC{\equiv}CH$ (1.733).

All calculations of $\Delta H^0{}_f$ were performed by the additive scheme.[11]

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