Full Articles

Theoretical analysis of hydrogen atom abstraction reactions by radicals within the framework of generalized Polanyi—Semenov relationship taking into account the formation of pre- and post-reactive complexes

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Density functional theory was used to calculate the intrinsic reaction coordinate of hydrogen atom abstraction from a number of organic molecules of different classes by C_7F_{15} radical. These reactions involve the formation of stable pre- and post-reactive complexes with binding energies comparable to the activation barriers and reaction energies. An analysis of the results obtained using the dimensionless reaction coordinate showed that the generalized Polanyi—Semenov relationship $E_a = A + 0.5\Delta H + \Delta H^2/(2W)$ is fulfilled. For primary and secondary C—H bonds of esters and ketones, it reproduces the calculated activation energies with an error of at most 1 kcal mol^{-1} provided $A = 8.5$ kcal mol^{-1} and $W = 43$ kcal mol^{-1}. The accuracy of the generalized Polanyi—Semenov relationship decreases when the enthalpy difference between the pre- and post-reactive complexes is used as the ΔH value because, as a rule, the structures of these complexes are not directly related to the structure of the transition state.

Key words: density functional theory, reaction coordinate, radical reactions, hydrogen transfer, pre-reactive complex, post-reactive complex, generalized Polanyi—Semenov relationship.

Hydrogen abstraction reactions play a fundamental role in chemical and biological processes.[1] Accordingly, numerous attempts were undertaken to develop a method of systematic theoretical description of these reactions in order to establish the effects of the key factors including the energies of the broken and newly forming bonds on the energy barriers and characteristics of the transition state (TS).[2,3] Historically, the Evans—Polanyi approach was initially introduced.[4] It was extended by N. N. Semenov[5] to reactions of hydrogen abstraction by radicals. The method gives a linear relationship between the activation energy E_a and the heat of reaction ΔH:

$$E_a = A + \alpha\Delta H, \qquad (1)$$

where α is the Brønsted coefficient characterizing the position of TS on the reaction coordinate.[6] The α values close

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to 0 and 1 are realized for the early (reactant-like) and late (product-like) TS, respectively. In addition, the activation energy A of a thermally neutral reaction is a measure of the chemical inertness, which is characterized by an internal barrier, and the chemical reaction is driven by the energy difference ΔH between the broken and newly formed bonds.[7]

A main consequence of the Polanyi—Semenov equation is that the kinetic and thermodynamic contributions to the activation energy of a reaction can be separated. However, linear correlations have an intrinsic drawback because quantification of related reactions requires the introduction of different parameterizations.[8] Attempts to improve the situation by introducing additional theoretical and empirical correlation parameters lead to complicated expressions (see, *e.g.*, Ref. 9). There exist even more complicated (in fact, nonlinear) theoretical models for *a priori* evaluation of activation energies, which make it possible to obtain good agreement with the results of exact calculations or experimental data. However, they remain of limited use because of the need for performing special calculations, and, which is important, the use of not only the enthalpy of reaction, but also additional experimental data.[10]

At the same time, a chemical experience shows that close changes in the molecular structure cause close changes in reactivity. This gives an impetus to search for simpler phenomenological approaches. Among them, there are the generalized Polanyi—Semenov model[11] and the model of crossing parabolas,[12,13] which lead to a quadratic dependence of E_a on ΔH.

As follows from general considerations, the total energy of reactants is a quadratic function of the displacement along the reaction coordinate in the vicinity of TS. Taking reactions of alkyl radicals with alkanes

$$\mathrm{AH + B \longrightarrow A + HB},$$

as examples, it was shown[12] that, using the reduced dimensionless reaction coordinate q*, this function has the following approximate form in the vicinity of TS ($q = 1/2$)

$$E(q) \cong A + q\Delta H^\circ - (W/2)(q - 0.5)^2, \qquad (2)$$

where A is the activation energy of a thermally neutral reaction, ΔH° is the classical enthalpy of reaction (enthalpy of reaction at $T = 0$ K minus the contribution of the zero-point energy), W is the curvature of the activation barrier, which is independent of A and ΔH° (see expression (2)). Note that the change in the enthalpy at $T = 0$ K is identical to the change in the energy. The function $E(q)$ takes its maximum value at the point

$$q^\# = 0.5 + \Delta H^\circ/W. \qquad (3)$$

Substituting $q^\#$ into relation (2) leads to quadratic dependence of the classical activation energy $E_a{}^\circ$ on the classical enthalpy of reaction ΔH° (generalized Polanyi—Semenov relationship):

$$E^\circ{}_a = A + 0.5\Delta H^\circ + (\Delta H^\circ)^2/(2W). \qquad (4)$$

Considering A and W as empirical parameters having constant values for a certain family of reactions, expression (4) becomes an efficient tool for prediction of the activation barriers to reactions of hydrogen atom abstraction by radicals with the known enthalpies. For instance, a less general one-parameter model of crossing parabolas[13] in which the parameters A and W are interrelated ($W = 8A$) has a rather high predictive power.

At the same time, owing to the existence of universal long-range attractive forces between any neutral molecular systems, for each reaction to be considered there exist some pre- and post-reactive complexes. Therefore, the classical enthalpy of reaction can be calculated using two possible physically different methods, namely, relative to the noninteracting reactants and reaction products (ΔH°) and relative to the pre- and post-reactive complexes ($\Delta\tilde{H}^\circ$). If reactants have low polarities, the energies of formation of such complexes are low and the corresponding energy differences are still less small. However, the situation changes in the case of polar reactants, namely, the ΔH° and $\Delta\tilde{H}^\circ$ values become different. Therefore, one should theoretically analyze which correlations, *viz.*, based on ΔH° or $\Delta\tilde{H}^\circ$, are more accurate.

This problem is not only methodologically important. In particular, it is also important for the description of the reactions of chain transfer to solvent in the case of telomerization of tetrafluoroethylene (TFE), because the energies of formation of such complexes become comparable with the activation energies of the reactions of hydrogen atom abstraction by radicals.[14,15] Owing to practical importance of the synthesis of TFE oligomers with specified properties, the development of a reliable *a priori* method of evaluation of the rate constants for chain transfer reactions is topical. Therefore, we studied reactions between the growing poly(tetrafluoroethylene) radical and various telogens.

Prior to analyzing the results obtained, mention should be made of the procedure for the choice of the dimension-

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* It should be noted that the introduction of the dimensionless reaction coordinate, which varies between 0 and 1, is essential. For instance, a simple scaling of the quantum chemically determined potential energy profile along the reaction coordinate is in principle impossible. The reaction coordinate varies in a very wide range which is first of all determined by the asymptotics of the interaction between reactants. Therefore, the extent of contraction of a rather small "invariant" region in the vicinity of TS in the case of simple scaling will mainly depend on the rate of changes in the potential energy at long distances between reactants rather than the TS parameters. If the initial and final states of a system are represented by noninteracting reactants and products, respectively, the reaction coordinate becomes infinitely long which makes a simple scaling problematic.

less reaction coordinate q. This is a known procedure taken from Ref. 11 and illustrated in Fig. 1 for the case where the initial and final states of the system are represented by the pre- and post-reactive complexes, respectively. First, the reaction coordinate is projected on the plane in which both r_{AH} and r_{HB} lie. The crossing of the tangent to the projected reaction coordinate with the lines $r_{AH} = r_{AH}{}^e$ and $r_{HB} = r_{HB}{}^e$ ($r_{AH}{}^e$ and $r_{HB}{}^e$ are the equilibrium bond lengths in the product and reactant, respectively) at the point corresponding to TS ($r_{AH}{}^{\#}$, $r_{HB}{}^{\#}$) gives the segment 0—1. Then, using two focuses f_a and f_b (see Fig. 1), a correspondence is established between any point of the reaction coordinate x and a point in the 0—1 segment; the relative position of the latter point is the q value. It is important that this procedure for the choice of q leads to a slight distortion of the profile of the potential energy surface (PES) in the vicinity of TS. The parameter W is completely determined by the PES properties in the vicinity of TS. In a particular case where the pass through the TS mainly involves transfer of H atom, one has

$$W \approx k^{\#}(\Delta r_{AH} + \Delta r_{HB})^2, \qquad (5)$$

where Δr_{AH} and Δr_{BH} are the elongations of the broken and newly formed bond, respectively, and $k^{\#}$ is the force constant of the vibration with the imaginary frequency in the TS.

All quantum chemical calculations were carried out within the density functional theory using the PBE functional,[16] an extended basis set for the SBK pseudopotential,[17] and the PRIRODA program[18] at the Joint Super-Computer Center, Russian Academy of Sciences. Reactions of C_7F_{15} radical with different C—H bonds in ethanol, methanol, THF, diethyl ether, acetone, methyl ethyl ketone, propionaldehyde, ethyl acetate, and formic acid dimer molecules were studied. The activation barriers, the energies of formation of the pre- and post-reactive complexes, the energies of reactions, and the geometric parameters of TS are listed in Table 1. Note that the calculated activation energy values are in qualitative agreement with the experimental data.[14] If the activation barriers are low (propionaldehyde, alcohols, THF, diethyl ether), one deals with fast chain transfer to solvent in the radiation-induced polymerization of TFE. Therefore, one can expect the formation of short-chain telomers $H(C_2F_4)_nR$ only in these solvents. In other cases, the activation barriers are higher and the formation of long-chain oligomers is expected. Indeed, the apparent n value increases to at least ten. The properties of telomer solutions, in particular, their ability to undergo gelation, depend strongly on the average n value. Therefore, the possibility of theoretical prediction of large and small n values in radiation-induced polymerization of TFE is of interest and topical.

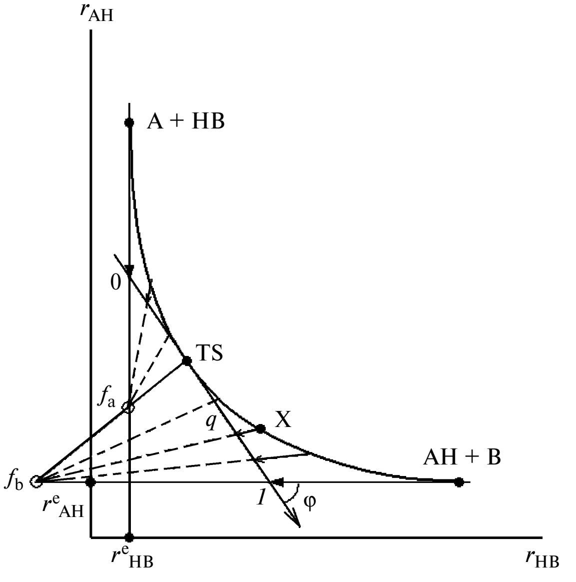

Fig. 1. Projection of the reaction coordinate, the functions of the distances r_{AH} and r_{HB}, on the segment 0—1; TS is transition state.

An example of the calculated PES profile along the reaction coordinate for diethyl ether and the corresponding TS structure is shown in Fig. 2. As can be seen, the region in the vicinity of TS spans only ~5% of the length of the reaction coordinate from the pre- to the post-reactive complex. After projection of the energy profile on the dimensionless coordinate q, two cases were considered. First, we subtracted the linear contribution $q\Delta E^\circ$ proportional to the classical energy of reaction ΔE°. In the second case, the contribution proportional to the classical energy difference between the pre- and post-reactive complexes $\Delta\tilde{E}^\circ$ was subtracted. The energy profiles thus obtained become dome-shaped (Fig. 3).

It should be emphasized that the energy changes for the reactions studied vary over a wide range from −11.6 to 3.6 kcal mol^{-1}. However, after "normalization" of the energy profiles of reactions using the procedure mentioned above, all curves approach one another and differ by at most 2 kcal mol^{-1}. Thus, the fundamental assumption that the energy effect of a reaction is linearly related to the shape of the potential barrier (*i.e.*, that relation (2) is valid) holds to a good accuracy for related reactions. This creates prerequisites for fast *a priori* calculations of the activation barriers to reactions based on the energy difference between the broken and newly formed bonds and the parameters A and W.

Figure 3 shows that the scatter of the curves in the case of subtraction of the contribution $q\Delta E^\circ$ is larger than in the case of subtraction of the contribution proportional to $\Delta\tilde{E}^\circ$. A comparison of other reactions considered leads to a similar situation. An analysis of the structure of the pre- and post-reactive complexes shows that only in a few cases they are to some extent structurally similar to TS, being different in C—H distances. Therefore, generally, they are not directly related to the reaction site and the energies of their formation characterize interactions with distant polar groups. This is just the reason for lower accuracy of

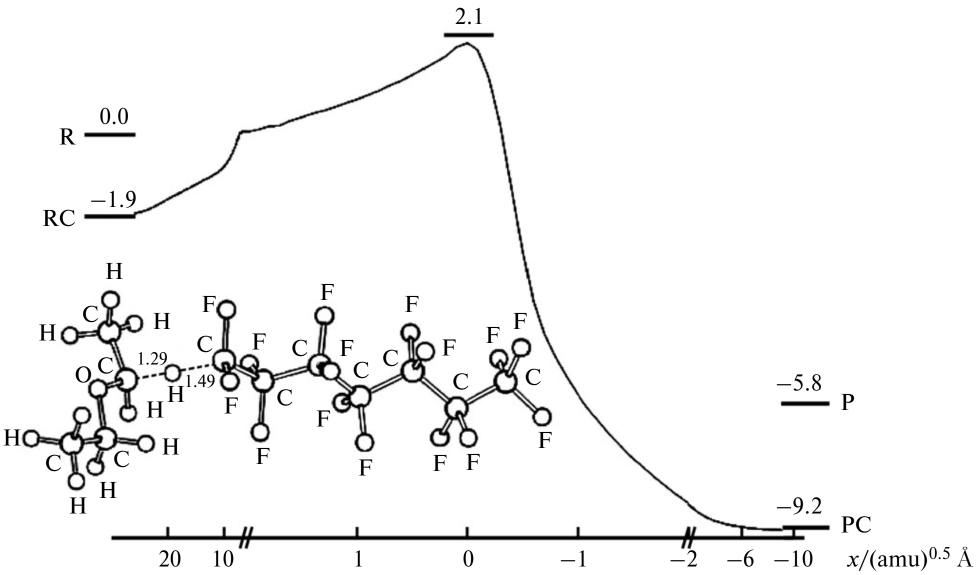

Fig. 2. Energy profile of the reaction of hydrogen atom abstraction from C_α-position of diethyl ether molecule. The energies are given in kcal mol^{-1} and calculated relative to the total energy of reactants. Double slashes denote the points at which the scale length along the abscissa axis changes. Inset: the structure of TS; shown are the interatomic distances (Å). Notations: R is reactants, RC is the pre-reactive complex, TS is transition state, PC is the post-reactive complex, P is reaction products, and *x* is the reaction coordinate.

correlations (large scatter of the energies of thermally neutral reaction *A* for very close C—H bonds. Thus, to use the generalized Polanyi—Semenov relationship, it is sufficient to know the energy characteristics of the reaction studied.

The results of analysis of all reactions considered in this work are summarized in Table 1 which also includes the positions of maximum α, the maximum *A* values, and the energy coefficients *W* for both types of application of the generalized Polanyi—Semenov relationship. In all cases, the α value is rather close to 0.5 (see Table 1) while the α averaged over all reactions is almost equal to 1/2. The difference between the average value of the calculated energy coefficient (43.2 kcal mol^{-1}) and the averaged *W* values determined from the analysis of the energy profiles of the reactions is at most 4%. The only difference consists in a large scatter of the theoretically determined values.

Except the reactions at the activated C—H bonds of propionaldehyde and formic acid dimer, the remaining data describe reactions at the primary and secondary C—H bonds of various telogens. They are clearly classified in two groups with respect to the magnitude of the parameter *A*. For C_α—H bonds in THF and diethyl ether, as well as

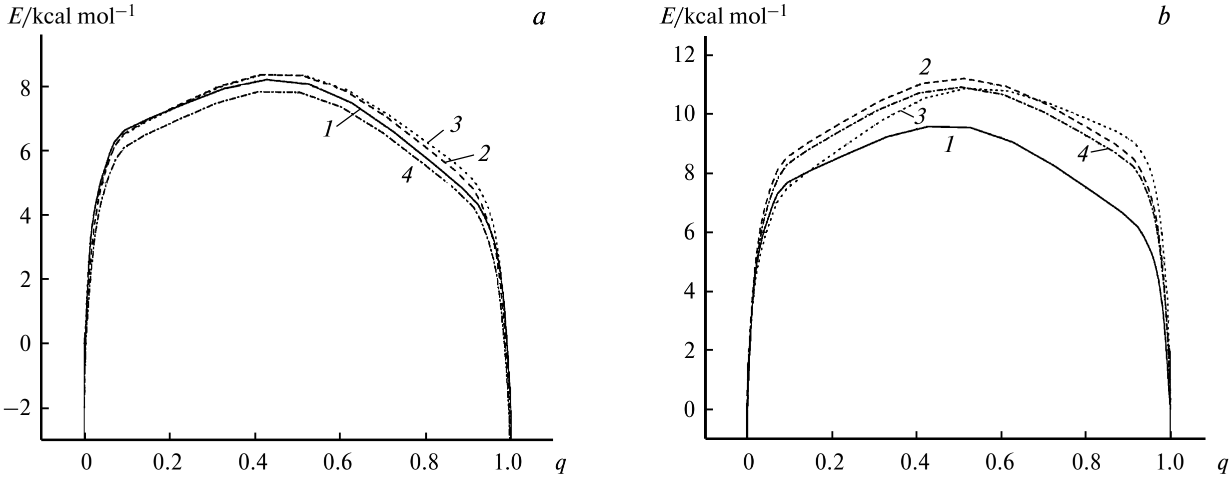

Fig. 3. Energy profiles of hydrogen atom abstraction from the C_β—H bond of propionaldehyde (*1*, *2*) and ethyl methyl ketone (*3*, *4*) in *trans*- (*1*, *3*) and *gauche*-positions (*2*, *4*) relative to the C—C bond after subtraction of the contribution proportional to the energy of reaction (*a*) and to the energy difference between the post- and pre-reactive complexes (*b*).

Table 1. Parameters of radical reactions[a]

Molecule	$-\Delta E_{pre}$	E_{act}	E°_{act}	$-\Delta E_{post}$	ΔE_{react}	ΔE°_{react}	$R^\#$		$^1\alpha$	^1A	^1w	$^2\alpha$	^2A	^2w	w_{calc}
							C—H	CF_2—H							
$C_2H_5C(O)$—$\underline{H}$	1.4	−2.6	−0.2	2.5	−9.9	−10.6	1.27	1.55	0.54	4.4	48	0.57	6.5	46	19
(HCOOH)($\underline{H}$—COOH)	1.4	5.0	8.3	2.5	1.5	1.6	1.37	1.38	0.47	7.5	47	0.49	9.5	47	53
$\underline{H}$—CH_2OH	2.0	1.1	3.4	3.2	−4.3	−3.9	1.32	1.44	0.49	5.1	42	0.52	8.1	42	40
$CH_3(CH$—$\underline{H})OH$	2.2	−0.9	1.8	3.7	−6.3	−5.8	1.29	1.48	0.48	4.2	40	0.53	7.3	40	30
$(CH_3CH$—$\underline{H})OC_2H_5$	1.7	−0.7	2.1	3.2	−6.3	−5.8	1.29	1.49	0.49	4.6	45	0.53	7.2	45	31
α-C—$\underline{H}(C_4H_8O)$	1.3	−2.2	0.3	3.5	−7.7	−7.5	1.28	1.51	0.51	3.5	32	0.58	6.2	34	24
$CH_3C(O)O(CH$—$\underline{H})CH_3$	1.3	2.9	6.0	4.5	−4.4	−3.4	1.32	1.43	0.48	7.5	46	0.55	10.6	46	51
$CH_3(CH_2$—$\underline{H})CO$	2.0	4.6	7.0	4.6	−3.7	−3.7	1.32	1.42	0.50	8.8	43	0.57	12.4	42	43
$(CH_2$—$\underline{H})C(O)C_2H_5$	2.1	4.3	6.8	4.5	−3.7	−3.8	1.32	1.41	0.50	8.5	35	0.59	12.1	36	42
$(CH_2$—$\underline{H})C(O)OC_2H_5$	2.2	5.3	8.0	4.5	−2.0	−1.8	1.33	1.39	0.49	8.8	41	0.56	12.3	36	46
$CH_3(CH$—$\underline{H})C(O)H$	1.7	1.9	4.5	4.2	−11.5	−11.6	1.27	1.50	0.57	9.7	48	0.63	13.1	37	32
$CH_3C(O)(CH$—$\underline{H})CH_3$	1.8	1.5	4.2	4.2	−10.6	−10.3	1.28	1.49	0.56	8.9	45	0.63	12.6	34	33
$(CH_2$—$\underline{H})CH_2OH^b$	2.4	6.2	9.3	3.3	1.4	2.3	1.37	1.35	0.47	8.1	42	0.49	11.1	43	50
$(CH_2$—$\underline{H})CH_2OH^c$	0.9	7.6	10.7	3.3	1.4	2.3	1.38	1.34	0.49	9.5	43	0.55	11.8	41	49
$(CH_2$—$\underline{H})CH_2OC_2H_5{}^b$	1.9	6.0	9.0	4.1	2.3	3.5	1.37	1.36	0.43	7.3	41	0.49	10.5	43	51
$(CH_2$—$\underline{H})CH_2OC_2H_5{}^c$	1.6	7.6	10.7	4.1	2.3	3.5	1.38	1.34	0.46	8.9	44	0.52	12.1	43	50
$CH_3C(O)OCH_2(CH_2$—$\underline{H})^b$	2.1	7.0	10.0	2.8	2.4	3.6	1.38	1.35	0.44	8.3	44	0.49	10.2	45	51
$CH_3C(O)OCH_2(CH_2$—$\underline{H})^c$	2.0	7.8	11.0	2.9	2.4	3.6	1.38	1.34	0.46	9.2	44	0.48	11.7	44	51
β-C—$\underline{H}(C_4H_8O)$	2.1	3.1	6.1	4.4	−3.4	−2.3	1.33	1.40	0.49	7.1	41	0.55	10.9	38	45
$(CH_2$—$\underline{H})CH_2C(O)H^b$	1.8	6.8	9.6	3.6	1.4	2.6	1.37	1.36	0.45	8.4	43	0.50	11.2	44	51
$(CH_2$—$\underline{H})CH_2C(O)H^c$	0.9	7.0	10.0	1.5	2.5	3.7	1.38	1.35	0.44	8.2	42	0.47	9.60	43	50
$CH_3C(O)CH_2(CH_2$—$\underline{H})^b$	2.0	6.2	9.1	3.9	1.4	2.5	1.37	1.36	0.45	7.9	42	0.50	10.9	44	51
$CH_3C(O)CH_2(CH_2$—$\underline{H})^c$	1.0	6.7	9.6	4.0	1.4	2.5	1.37	1.36	0.46	8.4	42	0.55	10.9	40	50

[a] ΔE_{pre}, E_{act}, E°_{act}, ΔE_{post}, ΔE_{react} and ΔE°_{react} are respectively the energy of formation of the pre-reactive complex, the activation energy calculated relative to the total energy of reactants, the classical activation energy calculated relative to the total energy of reactants, the energy of formation of the post-reactive complex, the energy of reaction and the classical energy of reaction (in kcal mol^{-1}); $R^\#$(C—H) and $R^\#(CF_2$—H) are the C—H bond lengths in the transition state; α, A, and w are the coordinate of the maximum, the maximum energy value, and the curvature of the potential energy profile as function of the reduced coordinate at the point of maximum (multiplied by −1) minus the contribution proportional to the classical energy of reaction (subscript 1) and the energy difference between the post- and pre-reactive complexes (subscript 2); w_{calc} are the estimates obtained using Eq. (5). All bond lengths are given in Å; α is the dimensionless parameter.

[b] Hydrogen atom in *gauche*-position relative to the adjacent group.

[c] Hydrogen atom in *trans*-position relative to the adjacent group.

C—H bonds in alcohols adjacent to the hydroxyl group the parameter A lies between 3.5 and 5.1 kcal mol^{-1}. In other cases, it falls into the range from 7.1 to 9.7 kcal mol^{-1}. Note that the formation of short-chain telomers is expected for those solvents for which group-I reactions are possible. Only group-II reactions are possible for esters and ketones; for these solvents, the formation of long-chain telomers is observed. The averaged values are as follows: $A = 4.3$ kcal mol^{-1}, $W = 40$ kcal mol^{-1} for the group-I reactions and $A = 8.45$ kcal mol^{-1}, $W = 42.8$ kcal mol^{-1} for the group-II reactions. Using these values, the activation energies are calculated with an error of at most 1 kcal mol^{-1}. Thus, the generalized Polanyi—Semenov relationship (4) with these parameter values can be recommended for practical use in assessing the reactivity of molecules.

An analysis of the reactions of perfluoroalkyl radical with C—H bonds of different organic molecules revealed that the structures of the pre- and post-reactive complexes are usually determined by the interactions of polar groups distant from the reaction site. Therefore, orientations of reacting C—H bonds in such groups are not related to the orientations of C—H bonds in the transition states. As a result, the use of the enthalpy difference between the pre- and post-reactive complexes in the generalized Polanyi—Semenov relationship introduces an uncontrollable systematic error and reduces its accuracy. One can also expect a similar situation for other radical reactions between polar reactants, *e.g.*, the formation of the pre- and post-reactive complexes will be controlled by hydrogen bonds and thus in most cases one should use the enthalpy of reaction in the generalized Polanyi—Semenov relationship.

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