Theoretical Analysis of Reactions of Electrophilic Iodination and Chlorination of Benzene and Polycyclic Arenes in Density Functional Theory Approximation

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Abstract—Quantum-chemical method DFT B3LYP/6-311G* was applied to stage by stage thermodynamic calculation of reactions of electrophilic iodination of benzene, naphthalene, phenanthrene, and anthracene with iodine and iodine monochloride, and comparison with chlorination reactions was performed. The main distinction of iodination process from chlorination was an enhanced reversibility owing to protodeiodination. The reversibility of iodination grows with the electron-donor properties of aromatic substrates. The calculations permit an assumption that the chlorination of anthracene and phenanthrene with iodine monochloride occurs most probably through stages of electrophilic iodination-dehydroiodination.

Iodine derivatives of aromatic and heteroaromatic compounds are among the most widely applied building blocks in the organic synthesis (see, for example, [1–3]). Yet the direct electrophilic iodination involves many problems, the main among them is according the common viewpoint the low electrophilicity of iodine and its active intermediates as compared with the other halogens [4, 5]. However the iodination is known to be hampered not only with deactivated aromatic substrates but on the contrary with very active compounds, e.g., fused aromatic hydrocarbons. For instance, anthracene and phenanthrene do not undergo iodination by reagents sufficiently active with respect to, e.g., less electron-donor alkylbenzenes [4]. Another spectacular example is the comparison of phenanthrene with the relatively deactivated phenanthrenequinone that unlike its more active precursor undergoes iodination with many reagents [4, 6]. Moreover, under the treatment of phenanthrene and anthracene with iodine monochloride occurred not iodination but chlorination [7, 8]. We also recently demonstrated that the "proper" electrophilicity of iodinating reagents XY (X = Cl, N, O; Y = I) is very close to the electrophilicity of the corresponding chloro- and bromoderivatives [9].

Thus the reduced electrophilicity of iodine and its active agents alone cannot explain the mentioned facts.

At the same time the problem of the reversibility of the electrophilic iodination is not investigated in detail as one of the probable reasons hampering the formation of aromatic iodides, and the publications touching this topic are fairly contradicting. For instance, in reviews [4–6] in the evaluation of the results of the electrophilic iodination its reversibility was not at all taken into consideration or was substituted by a discussion of the "reductive" role of hydroiodic acid that liberated in the course of iodination.

$$ArH + I_2 \longrightarrow ArI + HI$$
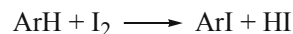
Moreover in some reports this possibility is rejected based on the study of Kekule who has found that iodobenzene is reduced at prolonged heating with HI only at 250°C [10]. However already in 1955 it was established by indirect experiments that ΔH of the reaction was negative and amounted to -5 kcal mol^{-1} [11], therefore the reaction was thermodynamically fully allowed. Besides, for instance, a sufficiently easy deiodination of 1,6-diiodo-2-methoxynaphthalene under the action of HI was described [12].

$$C_6H_5I + HI \longrightarrow C_6H_6 + I_2$$
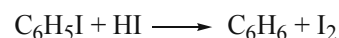
Deiodination effected by hydroiodic acid is not due to its known "reducing" ability, for iodoaromatic compounds loose iodine or undergo rearrangements also under the action of other strong acids. For instance, HCl caused the deiodination of iodoanilines [13] and the rearrangement of resorcinol (Jacobsen rearrangement) [14] or its methoxy derivative [15]. Under the action of H_2SO_4 isomerizations occurred of alkyliodobenzenes [16], iodobenzenes [17], and iodocarbazoles [18].

Hence it is possible to state that the deiodination of aromatic iodides in acid environment (protodeiodination) is a fairly frequent process with highly donor aryliodides.

$$ArI + H^+ \rightleftharpoons ArH + I^+$$

However the laws of these transformations are virtually unstudied and their contribution is unclear into the processes of direct iodination performed mainly in acid media.
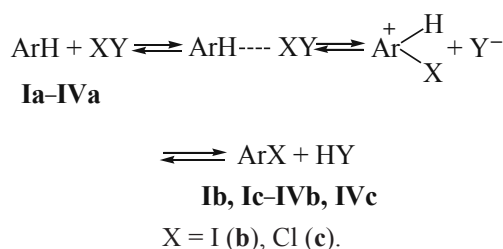
The target of this study is a quantum-chemical investigation with the Density Functional Theory method (DFT) B3LYP/6-311G* of the principal stages in the reactions of electrophilic iodination and for the sake of comparison, of chlorination of arenas in the gas phase and methanol solutions. The calculations in solutions were performed using a model of polarized continuum (overlapping-sphere model or Tomasi model) [19]. The calculations were carried out using a standard software package GAUSSIAN 98W [20]. For atoms H, N, C, O, F, and S a full-electron basic set 6-311G(d) was employed. The calculation were performed by hybrid method using density functional B3LYP together with Becke's exchange functional B3 [21] and correlation functional of Lee, Yang, and Parr (LYP) [22]. This method in now commonly used for description of thermodynamic characteristics. The geometry of all calculated molecules was completely optimized, the absence of imaginary vibration frequencies confirmed their stationary character. For iodine atom a relativistic potential was used including 46 hull electrons, and a basis set 6-311G* (10s9p5d) for valence electrons [23]. This basis set increases the flexibility in the region of valence electrons as compared to the basis 6-31G because it employs three functions for presentation of each atomic valence orbital. Dissociation energies of calculated compounds were corrected with accounting for the zero vibration energy (*ZPVE*) and brought to the standard conditions (298.15 K, 1 at) using the thermal correction for enthalpy and free energy.

We selected as substrates benzene (**Ia**) and its polycyclic derivatives: naphthalene (**IIa**), phenanthrene (**IIIa**), and anthracene (**IVa**). These compounds differ significantly in activity and chemical behavior in reactions with iodine-containing agents. As the latter we chose iodine, iodine monochloride, and chlorine as a chlorinating agent.

Complete optimization of structure was performed for initial substrates **Ia–IVa**, reagents XY (I_2, ICl, and Cl_2), molecular or π-complexes of substrates with I_2, ICl, and Cl_2, and also of intermediate σ-complexes and the corresponding halogenation products, hydrocarbons substituted with iodine and chlorine **Ib, Ic–IVb, IVc**, formed along Scheme 1. In the case of naphthalene isomeric 1- and 2-halides were investigated.

Scheme 1.

$$ArH + XY \rightleftharpoons ArH\text{----}XY \rightleftharpoons Ar\overset{+}{\underset{X}{\overset{H}{<}}} + Y^-$$

Ia–IVa

$$\rightleftharpoons ArX + HY$$

Ib, Ic–IVb, IVc

X = I (**b**), Cl (**c**).

The structures of the corresponding σ-complexes are presented on Scheme 2.

Scheme 2.
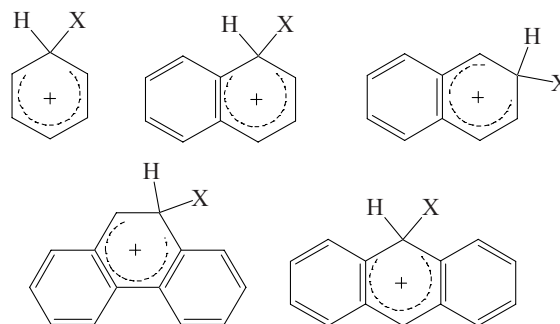
The calculated structures of π-complexes are of a single type and are characterized by the axial position of XY molecules to the plane of aromatic donors at angles of 90–100°. Some structural parameters of the π-complexes are given in Table 1, and in Tables 2–4 are compiled their thermodynamic parameters of formation.

The validity of the performed calculations are confirmed by the likeness of the calculated structures of the π-complexes and their heats of formation ΔH_{compl} to the known experimental and calculated data (see, e.g., [24–26]). For instance, the experimentsl values of ΔH_{compl} for ICl with benzene and its derivatives equal −1.4 ...

−4.3 kcal mol^{-1} [27] sufficiently close to the calculated values (Tables 2–4).

The calculated bond lengths l of the free acceptors XY (I–I 2.721, I–Cl 2.385, Cl–Cl 2.057 Å) are in a fair agreement with the experimental values (I–I 2.666, I–Cl 2.321, Cl–Cl 1.988 Å). As should be expected, the same bonds lengthen in the π-complexes (Table 1), but in general no correlation is observed between the bond lengths X–Y in π-complexes and their strength (Tables 1–4).

At increased polarity of the medium (methanol) the stability of the π-complexes somewhat grows as compared to the gas phase, but the values ΔH_{compl} and

Table 1. Calculated distances between X and the nearest carbon atom of the ring (X···C^i) and bond lengths X–Y (Å) in π-complexes of arenes **Ia–IVa** in gas phase

Arene	I$_2$		Cl$_2$		ICl	
	X···C^i	X–Y	X···C^i	X–Y	X···C^i	X–Y
Benzene	3.326	2.742	2.970	2.088	3.129	2.420
Naphthalene[a]	3.681	2.728	4.791	2.057	3.391	2.403
Phenanthrene[b]	3.339	2.752	3.086	2.091	3.132	2.434
Anthracene[c]	3.278	2.756	3.102	2.094	3.032	2.443

Numbers of carbon atoms: [a] $i = 4a$, [b] $i = 4$ (I$_2$, ICl), $i = 9$ (Cl$_2$), [c] $i = 9$.

Table 2. Thermodynamic parameters of reaction of arenes **Ia–IVa** with I$_2$ in gas phase and in methanol solution calculated by method B3Lyp/6-311G*, kcal mol^{-1}

| Parameter	Benzene	Naphthalene (position 1)	Naphthalene (position 2)	Phenanthrene	Anthracene
ΔH_{compl}	−1.72	−0.04	−0.04	−1.43	−0.79
$\Delta G_{compl\ solv}$	−4.09	−0.56	−0.56	−2.92	−1.59
ΔH	11.49	12.93	11.57	13.46	15.40
ΔH_σ	144.66	128.83	130.91	124.64	114.35
ΔG	11.73	13.28	11.80	13.70	15.35
ΔG_{solv}	11.84	15.77	13.35	15.10	17.90
ΔG_σ	145.02	130.97	132.92	125.29	115.47
$\Delta G_{\sigma\ solv}$	29.21	17.72	23.50	19.87	8.94

Table 3. Thermodynamic parameters of reaction of arenes **Ia–IVa** with Cl$_2$ in gas phase and in methanol solution calculated by method B3Lyp/6-311G*, kcal mol^{-1}

Parameter	Benzene	Naphthalene (position 1)	Naphthalene (position 2)	Phenanthrene	Anthracene
ΔH_{compl}	−1.66	−1.11	−1.11	−1.26	−0.79
$\Delta G_{compl\ solv}$	−2.24	−0.17	−0.17	−4.05	−2.92
ΔH	−29.69	-28.66	−29.63	−28.30	−27.24
ΔH_σ	131.69	112.34	115.94	107.53	92.88
ΔG	−29.22	−28.13	−29.16	−27.77	−27.06
ΔG_{solv}	−32.13	−29.22	−30.01	−29.18	−26.50
ΔG_σ	123.48	112.94	116.58	108.12	93.62
$\Delta G_{\sigma\ solv}$	−7.32	−15.74	−12.17	−11.46	−28.31

Table 4. Thermodynamic parameters of reaction of arenes **Ia–IVa** with ICl in gas phase and in methanol solution calculated by method B3Lyp/6-311G*, kcal mol^{-1}

Parameter	Benzene	Naphthalene (position 1)	Naphthalene (position 2)	Phenanthrene	Anthracene
ΔH_{compl}	−3.60	−1.30	−1.30	−3.65	−3.33
$\Delta G_{compl\ solv}$	−5.91	−2.29	−2.29	−6.09	−2.91
ΔH	−5.14	−3.70	-5.06	-3.17	−1.23
ΔH_σ	143.31	126.86	128.93	123.30	113.66
ΔG	−4.41	−2.86	−4.34	−2.44	−0.79
ΔG_{solv}	−7.08	−3.16	−5.58	−3.83	−1.03
ΔG_σ	142.01	127.95	129.9	122.2	112.45
$\Delta G_{\sigma\ solv}$	12.98	1.48	17.26	83.63	−7.30

$\Delta G_{compl.solv}$ remain close to zero and vary irregularly depending on the arene structure. Besides the calculation showed that in keeping with the known results for iodine complexes with benzene [28] the minima of free energy for the studied π-complexes were located in a wide region, i.e., the variations in the structural parameters of the complexes led to insignificant changes in their energy. In other words, the π-complexes may exist as a set of structures slightly differing in the free energy. A scheme of variations in enthalpy and free energy of reactions with designation of the calculated parameters of reactivity is shown on the figure.
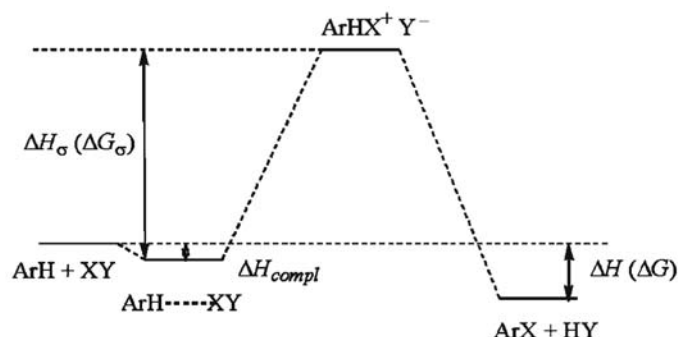
Variation of enthalpy and free energy in halogenation reactions of aromatic compounds **Ia–IVa** according to Scheme 1.

The calculated structures of σ-complexes in iodination and chlorination reactions are characterized by orthogonal position of the X–C–H plane with respect to the plane of the aromatic ring, namely, they are typical Wheland complexes. In Table 5 the following calculated parameter are given for the σ-complexes of arenes **Ia–IVa** with iodine: charges on iodine atoms [q(I)], bond lengths [d(C–I)], and bond angles ICH.

It is known that free I_2 in contrast to ICl under common condition of organic synthesis does not iodinate either of substrates **Ia–IVa**. This fact is traditionally ascribed to the low electrophilicity of I_2. However the comparison of calculated data for iodination and chlorination (Tables 2, 3) shows that the main difference in these reaction independent of the medium polarity lies in the thermodynamics (exothermal chlorination and endothermal iodination). On the other hand the same

thermodynamic factors suggest that the iodination with ICl of all studied substrates may occur both in nonpolar and polar environment (Table 4) in agreement with the experimental findings for benzene (**Ia**) and to certain degree, for naphthalene (**IIa**) [8]. The calculated results for iodination and chlorination of naphthalene (**IIa**) (Tables 2–4) are in total agreement with the classical concept on kinetic control of the electrophilic substitution into position *1* and thermodynamic control, into position *2*. These data also provide an understanding of the fact that the high-temperature oxidative iodination of naphthalene in the gas phase by iodine on zeolite KX at 225–350°C under the action of oxygen provided a mixture of compounds with 2-iodonaphthalene prevailing (65% of 2-isomer and 10% of 1-isomer of compound **IIb**) [29], whereas the iodination under common condition of organic synthesis (as a rule, below 100°C) resulted predominantly in the 1-iodonaphthalene [1]. To the least degree the equilibrium of the iodination is shifted to the right for phenanthrene and especially for anthracene. These substrates are known not to suffer iodination when treated with ICl [7, 8].

For each halogenation agents in both media the variation of the calculated heats of reactions (ΔH, ΔG, ΔG_{solv}) of compounds **Ia–IVa** and of energies of the σ-complexes (ΔH_{σ}, ΔG_{σ}, $\Delta G_{\sigma\ solv}$) (Tables 2–4) have opposite trends; thus the substrates highly active in electrophilic substitution should be most prone to protodeiodination.

The calculated activation barriers in the substrate series **Ia–IVa** for iodination and chlorination vary quite regularly: At growing electron-donor quality of substrate the values ΔH_{σ} and ΔG_{σ} decrease in the series benzene > naphthalene > phenanthrene > anthracene. Therewith a good linear correlation is observed of the calculated activation parameters in the gas phase with the potentials of electrochemical oxidation ($E_{1/2}$, V) of these aromatic substrates or with their ionization potentials (I, eV) [equations (1–6)].

Reaction with I_2:

$$E_{1/2} = \Delta 3.77 + 0.04\Delta H_{\sigma}, r\ 0.993, s\ 0.07 \qquad (1)$$

$$I = \Delta 0.63 + 0.07\Delta H_{\sigma}, r\ 0.996, s\ 0.09 \qquad (2)$$

Table 5. Characteristics of σ-complexes ArHI⁺

Parameter	Benzene	Naphthalene (position *1*)	Naphthalene (position *2*)	Phenanthrene	Anthracene
q(I)	0.319	0.255	0.273	0.243	0.174
d(C–I), Å	2.275	2.287	2.291	2.328	2.277
Angle ICH	99.900	99.9--	99.700	99.000	100.100

Reaction with ICl :

$$E_{1/2} = \Delta 3.65 + 0.04\Delta H_\sigma, \; r \; 0.993, \; s \; 0.07 \qquad (3)$$

$$I = \Delta 0.40 + 0.07\Delta H_\sigma, \; r \; 0.996, \; s \; 0.09 \qquad (4)$$

Reaction with Cl_2:

$$E_{1/2} = +2.12 + 0.03\Delta H_\sigma, \; r \; 0.995, \; s \; 0.06 \qquad (5)$$

$$I = 2.20 + 0.05\Delta H_\sigma, \; r \; 0.994, \; s \; 0.11 \qquad (6)$$

For naphthalene in equations (1–6) were used the values ΔH_σ for the substitution into position *1*, whereas the corresponding point for the substitution into position *2* deviated from the correlations. It is apparent that the variation of the substrates structure relatively less affects the change in the energy barriers to chlorination than to iodination both by the action of I_2 and ICl [slopes at ΔH_σ in equations (5, 6) and (1–4) equal 0.03 and 0.005 for chlorination and 0.04, 0.07 for iodination]. This circumstance corresponds to expected lower selectivity of chlorination compared to iodination.

The increase in the medium polarity at halogenation leads according to the calculations to the following results. The thermodynamics of the halogenation changes relatively weakly (1–3 kcal mol^{-1}) with the alteration of the medium polarity (cf. values ΔH, ΔG, and ΔG_{solv} in Tables 2–4) in conformity with low solvation energy of uncharged molecules of compounds under study (2–8 kcal mol^{-1}). On the other hand, the solvation energies in methanol of ionic species (σ-complexes, Cl$^-$, I$^-$) is reasonably bigger by an order of magnitude (45–75 kcal mol^{-1}). This fundamentally decreases the energy barrier of the reactions (cf. values ΔG_σ and $\Delta G_{\sigma \, solv}$ in Tables 2–4) up to negative $\Delta G_{\sigma \, solv}$ values for all the chlorination reactions, and also for the iodination of the anthracene effected by ICl. The performed calculation doubtlessly underestimate the value $\Delta G_{\sigma solv}$ since they utilize a simple model of "isolated", not interacting components [σ-complex]$^+_{solv}$ [Y]$^+_{solv}$. In this approximation the solvation energies of "isolated" ionic species, especially of the small chloride ion, prove to be big out of proportion compared with the solvation energies of actually existing transition states and σ-complexes where anion Y$^+$ is present in the common solvation shell with the organic cation [σ-complex$^+$ Y$^+$]$_{solv}$. This problem will be treated in detail in a separate study.

In the whole the analysis performed shows that the reversibility of the iodination process effected by iodine monochloride owing to protodeiodination of aryl iodides should make a significant contribution into the reaction result for the aromatic compounds with pronounced electron-donor characteristics, but not to prevent totally the iodination, i.e., iodine derivatives of naphthalene, anthracene, and phenanthrene under the action of ICl should form and exist in notable amounts in the mixture with initial arenas. However among the substrates under study only benzene is iodinated with iodine monochloride with an acceptable yield. Naphthalene treated with ICl in acetonitrile formed exclusively 1-chloronaphthalene (**IIc**) [7] and yielded only a small amount of 1-iodo-derivative **IIb** in sulfuric acid [8]. Anthracene and phenanthrene with ICl under various conditions formed only chlorinated derivatives **IIIc** and **IVc** [7, 8]. In other words, the results of this study do not give direct understanding of the "inertness" of anthracene and phenanthrene with respect to iodination under the action of ICl.

According to [7] naphthalene, anthracene, and phenanthrene form with ICl molecular complexes that by one-electron transfer easily decompose into cation-radicals of arene as, and the latter give the corresponding aryl chlorides by the reaction with chloride ion. Evidently, this process should compete with the common electrophilic substitution of these arene as by ICl and should possess lower activation characteristics and also be more favorable thermodynamically.

To estimate quantitatively the probability of this reaction pathway we carried out a calculation of the thermochemistry of the decomposition processes of the molecular complexes of anthracene and phenanthrene with ICl into ion-radical species in the gas phase (ΔH, ΔG) and in methanol (ΔG_{solv}) [equations (7 and 8)].

$$\text{Anthracene·ICl} > \text{Anthracene}^{+\cdot} + \text{ICl}^- \qquad (7)$$

$$\text{Phenanthrene·ICl} > \text{Phenanthrene}^{+\cdot} + \text{ICl}^- \qquad (8)$$

The obtained values of the changes in the free energy and enthalpy of the processes (anthracene: ΔH 101.52, ΔG 86.28, ΔG_{solv} 7.43, phenanthrene: ΔH 102.85; ΔG 97.78; ΔG_{solv} 18.49 kcal mol^{-1}) show that in nonpolar media the decomposition of the π-complexes into cation-radicals of anthracene and phenanthrene is thermodynamically very unfeasible. The increased polarity of the medium increases the probability of this decomposition, but still the values ΔG_{solv} remain positive. Thus the performed calculations do not confirm the deciding contribution of reactions (7a and 7b) into the formation of chlorophenanthrene (**IIIc**) and chloroanthracene (**IVc**) under the action of ICl.

An alternative probable route to 9-chloroanthracene (**IVc**) may involve a sequence of electrophilic addition-elimination (Scheme 3) with an intermediate formation

Scheme 3.
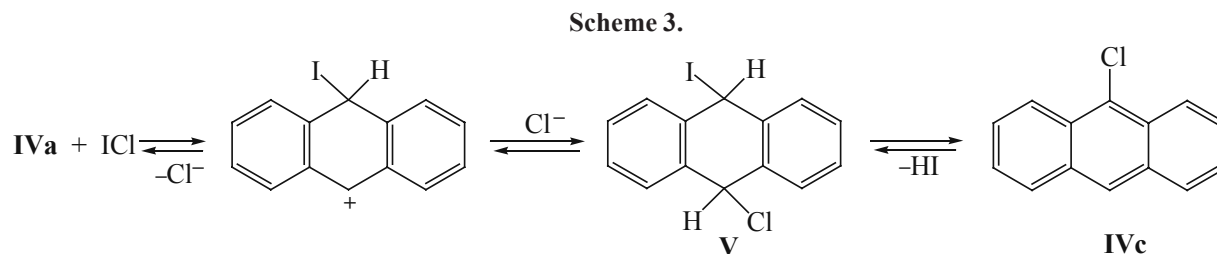
of 9-iodo-10-chlorodihydroanthracene (**V**); similar mechanisms have been formerly developed to explain some reactions of electrophilic substitution of anthracene, for instance, its chlorination with *N*-chlorosuccinimide [30].

According to performed calculations the formation of an intermediate 9-iodo-10-chlorodihydroanthracene (**V**) proved to be sufficiently thermodynamically probable in the gas phase and especially in the polar environment (methanol) (ΔH −3.56, ΔG 7.23, ΔG_{solv} −10.50 kcal mol^{-1}). The calculation of the thermodynamics of the reaction presented in Scheme 3 confirms on the whole its practicability (ΔH −4.18, ΔG −3.68, ΔG_{solv} −0.76 kcal mol^{-1}). During the experimental chlorination of anthracene with iodine monochloride the iodine elimination is known to occur [7], the of iodine might form in the stage of decomposition of the intermediate compound **V**, for example, through the transition state **VI** (Scheme 4).

Scheme 4.

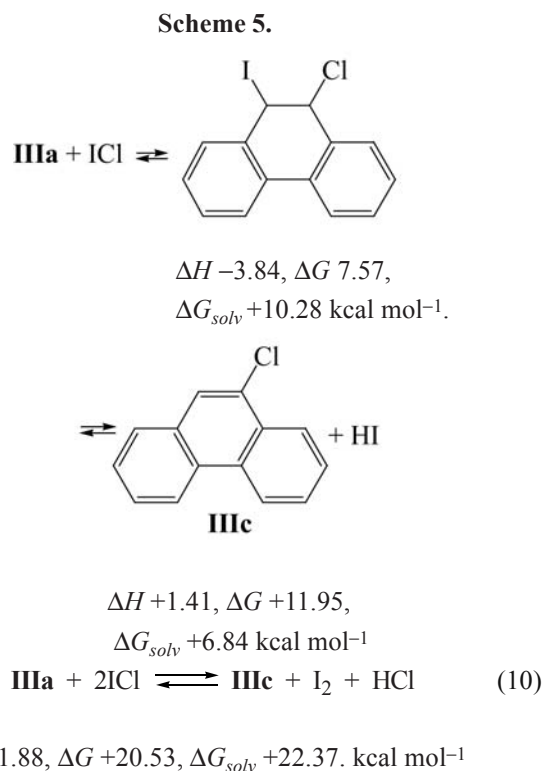ΔH −17.25, ΔG −27.05, ΔG_{solv} −9.19 kcal mol^{-1}.
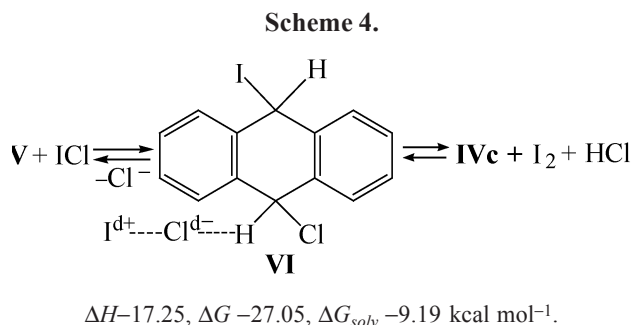
The consideration of the stage of iodine formation (Scheme 4) resulted in still greater thermodynamic feasibility of chloroanthracene (**IVc**) formation via intermediate **V**. On the whole the chlorination of anthracene with 2 mol of ICl [equation (9)] according to calculations proved to be fairly thermodynamically favorable (ΔH −20.81, ΔG −19.82 kcal mol^{-1}) and therewith weaky depending on the polarity of the environment (ΔG_{solv} −19.69 kcal mol^{-1}).

$$\textbf{IVa} + 2ICl \rightleftarrows \textbf{IVc} + I_2 + HCl \qquad (9)$$

The calculation of the phenanthrene chlorination with iodine monochloride through the stages of addition-

elimination predicted even higher than with anthracene thermodynamical probability of this reaction route [Scheme 5, equation (10)].

Scheme 5.

ΔH −3.84, ΔG 7.57,
ΔG_{solv} +10.28 kcal mol^{-1}.

ΔH +1.41, ΔG +11.95,
ΔG_{solv} +6.84 kcal mol^{-1}

$$\textbf{IIIa} + 2ICl \rightleftarrows \textbf{IIIc} + I_2 + HCl \qquad (10)$$

ΔH +21.88, ΔG +20.53, ΔG_{solv} +22.37. kcal mol^{-1}

Summing up the results obtained we can conclude that the reaction of the highly donor polycyclic arene is to a large degree controlled by thermodynamic factors. Therewith the calculations predict that the chlorination of anthracene and phenanthrene with iodine monochloride most probably proceeds through the stages of electrophilic iodination–dehydroiodination, but not through intermediate cation-radicals of anthracene and phenanthrene.

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