Physical Chemistry

A simple method for quantitative estimation of C—H bond lengths in hydrocarbon radical cations

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A quantitative correlation between deviations of the C—H bond lengths of hydrocarbon molecules during their adiabatic single ionization and isotropic hyperfine coupling constants with protons of their primary radical cations (RC) was established. A simple method for estimation of the C—H bond lengths of hydrocarbon RC was proposed on the basis of the correlation found. Specific features of the structure of the RC of methane and several *n*-alkanes of the general formula $[H^{*}(CH_2)_nH^{*}]^{\cdot +}$, $n = 0$ to 12, were analyzed. A widely used empirical rule, according to which deprotonation of hydrocarbon RC during the ion-molecular process is determined by the proton possessing the highest spin density, was refined and geometrically substantiated.

Key words: hydrocarbons, radical cations; geometric structure; isotropic hyperfine coupling constants.

At present, available information about geometric structures of hydrocarbon radical cations (RC) is random and often contradictory. The absence of practically convenient physicochemical methods for direct determination of the geometry of free radical systems forces us to use indirect estimations. Geometric parameters of hydrocarbon RC calculated by quantum chemical methods and necessary, in particular, for subsequent analysis of parameters of ESR spectra of radical cations are, in essence, the single available structural database. At the same time, the effect of matrix surroundings, intrinsic dynamics of the paramagnetic system, and insufficient adequacy of widely used quantum chemical approximations impede determination of structural parameters from ESR spectra by quantum chemical methods.

Only in some cases, were magnetic resonance parameters of hydrocarbon RC calculated by quantum chemical methods and those determined by radiospectroscopy matched, which made it possible to accept the geometry of RC used in calculations as "reliable" and corresponding to gas-phase conditions.[1,2] According to the reliable nonempirical calculations,[3—8] bond lengths and bond angles in σ-electronic RC, whose isotropic hyperfine coupling (IHFC) constants with protons are 50 to 250

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Oe, differ strongly from the corresponding values for neutral molecules[9] (several hundredths Å and tenths degrees). Similar calculation schemes are limited by small systems because of methodical reasons and are inappropriate for sufficiently complex hydrocarbon RC.[10] The geometry of initial molecules[2] can be used in calculations of π-type multiatomic RC with their inherent IHFC constants ($a^H_{iso} \leq 30$ Oe), because π-electronic RC, unlike σ-electronic ones, are characterized by relatively small structural distortions.

Since ESR spectra of paramagnetic systems contain sufficiently complete structural chemical information, we attempted in this work to establish a quantitative correlation between C—H bond lengths and IHFC constants a^H_{iso} of σ- and π-electronic RC on the basis of reliable experimental and theoretical data.[1–15] This correlation could allow one to determine empirically the C—H bond length in hydrocarbon RC on the basis of the geometry of the initial or similar molecule and the experimental IHFC constant with the corresponding proton in the given RC. Similar regularities can also be used for substantiation of the widely used empirical rule, according to which the center with the highest spin density is responsible for deprotonation of hydrocarbon RC.[14]

Results and Discussion

Primary RC are formed by a single adiabatic ionization of hydrocarbons. This process (1) is accompanied by structural changes, *e.g.*, changes in bond lengths, including C—H bond lengths (2). Correlation (3) between the increments of bond lengths Δ(C—H) (2) and IHFC constants a^H_{iso} with protons of these bonds was established for a thoroughly selected series of carbon RC. The values of C—H bond lengths in hydrocarbons and their RC were used. They were nonempirically calculated in the 6—31 G* and 6—31 G** bases, respectively, taking into account electronic correlation by the MP2 and CI methods.[3–6] IHFC constants a^H_{iso} were taken from experimental ESR spectra[8–10] and reliable *ab initio* calculations.[3–5]

Increments Δ(C—H), which accompany adiabatic ion-

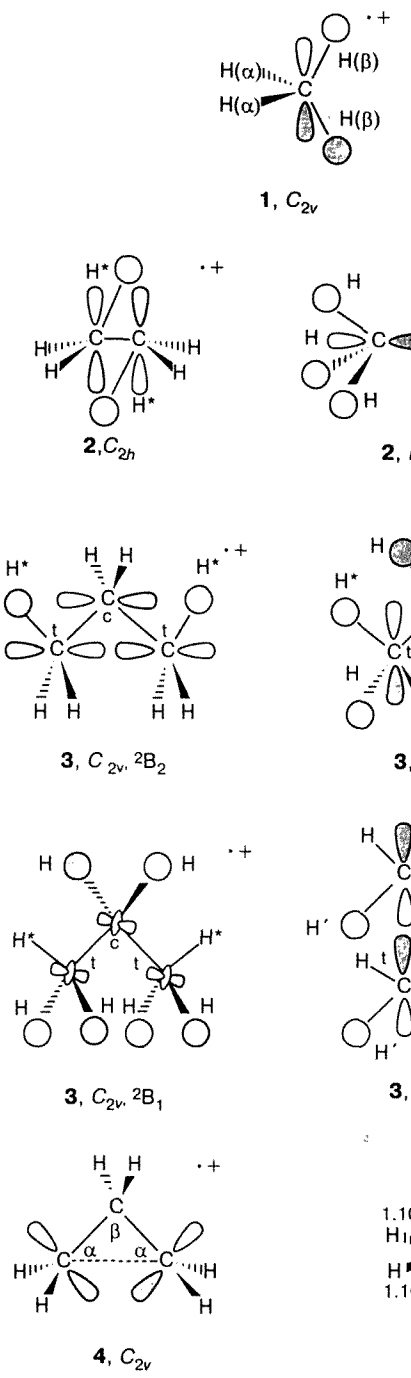
$$RH \xrightarrow{-\bar{e}} RH^{\cdot +} \qquad (1)$$

$$\Delta(C{-}H) = r(C{-}H^{\cdot +}) - r(C{-}H_{mol}) \qquad (2)$$

$$\Delta(C{-}H) = f(a^H_{iso}) \qquad (3)$$

ization of four selected hydrocarbons, determined with high accuracy and IHFC constants a^H_{iso} of their primary RC (σ-electronic RC of alkanes C_nH_{2n+2} with $n = 1$ to 3 and π-electronic RC *cyclo*-$C_3H_6^{\cdot +}$) are presented in Table 1. These values are compared in Fig. 1, and

Scheme 1



designations of atoms in RC are given in Scheme 1. Seven experimental points in Fig. 1 supplemented by twenty one calculated points reflect the dependence with a maximum of a^H_{iso} ~250 Oe at Δ(C—H) approximately equal to 0.08 Å. The dependence passes through the origin of coordinates and is approximated by two straight lines (Eqs. (4) and (5)) intersecting at the maximum

point.

$$a^{H}_{iso} = 3280 \cdot \Delta(C{-}H);\ \Delta(C{-}H) \leq 0.08\ Å \quad (4)$$

$$a^{H}_{iso} = -14000 \cdot \Delta(C{-}H) + 1310;\ \Delta(C{-}H) \geq 0.08\ Å \quad (5)$$

As seen from Fig. 1, shortening of the C—H bonds corresponds to negative (α) values of constants a^{H}_{iso} (whose absolute values do not exceed 23 Oe), while lengthening corresponds to positive (β) values. Up to $\Delta(C{-}H) \approx 0.08$ Å, lengthening of any C—H bond in hydrocarbon RC is accompanied by an increase in the spin density on the proton (Eq. (4)), and further lengthening of the C—H bond is accompanied by a sharp decrease in the spin density on the proton (Eq. (5)). IHFC constant $a^{H}_{iso} \approx$ 250 Oe corresponding to the maximum in Fig. 1 is lower in half than that of the isolated hydrogen atom (a^{H}_{iso} = 508 Oe).[11]

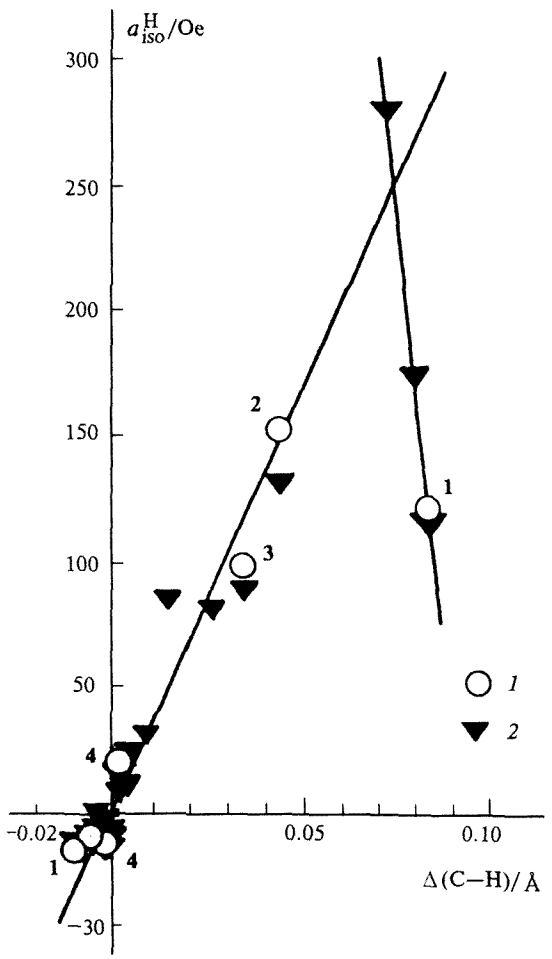


Fig. 1. Correlation between IHFC constants a^{H}_{iso} with protons and increments $\Delta(C{-}H) = r(C{-}H^{\cdot+}) - r(C{-}H_{mol})$ of C—H bond lengths of hydrocarbons upon their ionization (**1**—**4**, see Table 1): *1*, experiment; *2*, *ab initio* calculation.

It is likely that the curve with the maximum (see Fig. 1) is parallel to the dependence of the ionicity of the chemical C—H bond on its length. It is known[12] that changes in dipolar moments of some molecules and free radicals are characterized by similar dependences.

IHFC constants a^{H}_{iso} of σ-electronic RC of hydrogen, methane, and *n*-alkanes of general formula $C_nH^{\cdot+}_{2n+2}$ (n = 0 to 10) are presented in Table 2. The character of the change in these constants as n increases can be observed in Fig. 2. The dependence presented in Fig. 2 (straight lines *1*—*3*) can conventionally be divided into three regions (n = 0 to 4, n = 4 to 9, and $n \geq 9$). On each of these regions, the points fall almost exactly on the lines with different slopes, which reflect the decreases in IHFC by ~50, ~10, and ~0 Oe, respectively, as the chain lengthens by one carbon atom.

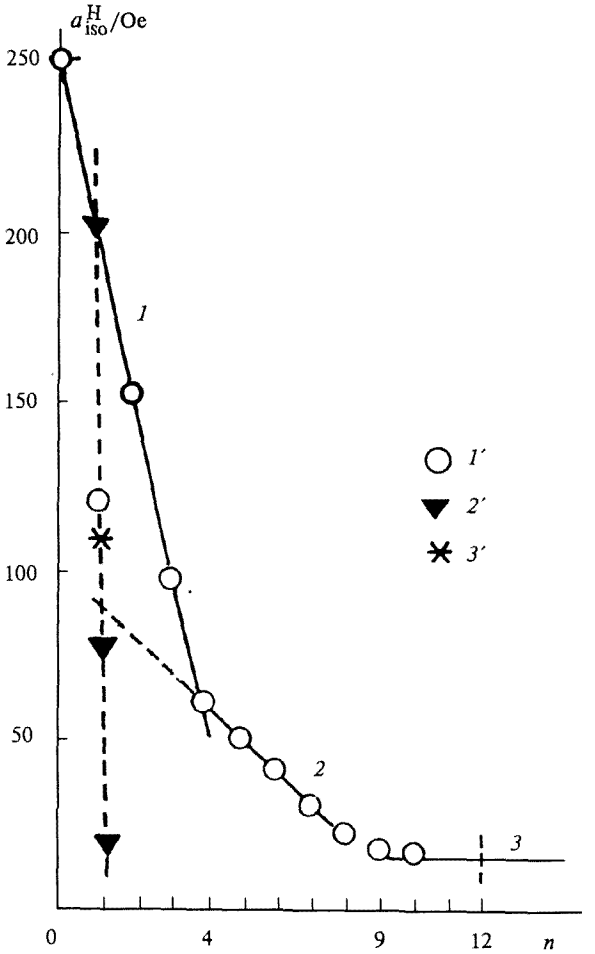


Fig. 2. Dependence of a^{H}_{iso} on n (*1*—*3*) in the series of RC of *n*-alkanes $[H^{*}(CH_2)_nH^{*}]^{\cdot+}$; C_nH^{*} atoms are localized in the same plane: *1*, n = 0 to 4; *2*, n = 4 to 9; *3*, n = 9 to 12; dashed line indicates experimental and estimated values of a^{H}_{iso} for $CH_4^{\cdot+}$ at n = 1. *1′*, experiment; *2′*, estimation from structural data of *ab initio* calculation; *3′*, average estimated value of a^{H}_{iso} for protons in the symmetry plane of $CH_4^{\cdot+}$ RC (see Scheme 1).

Table 1. Increments Δ(C—H) of C—H bond lengths that accompany adiabatic ionization of hydrocarbons and IHFC constants a^H_{iso} of their primary radical cations

RH (symmetry)	Bond	d /Å	$RH^{\cdot+}$ RC (symmetry)	Bond	d /Å	ΔC—H/Å (2)	a^H/Oe exp.	a^H/Oe *ab initio*
CH_4 **1**	CH	1.084	$CH_4^{\cdot+}$	CH	1.074	−0.010	−14.6	−11.1
$(T_d)^a$			$(C_{2v})^b$	CH	1.169	0.085	121.7	116.2
C_2H_6 **2**	CH	1.086	$C_2H_6^{\cdot+}$	CH	1.131	0.045	152.5	131.3
$(D_{3d})^a$			$(C_{2h})^c$	CH	1.081	−0.005	−9.0	−8.8
			$(D_{3d})^c$	CH	1.082	−0.004	—	0.1
C_3H_8 **3**	CH(t*)	1.086	$C_3H_8^{\cdot+}$	CH(t*)	1.121	0.035	98.0	88.6
$(C_2)^a$	CH(t)	1.087	$(^2B_2, C_{2v})^d$	CH(t)	1.087	0.000	—	−5.8
		1.087		CH(c)	1.088	0.001	—	−7.1
				CH(t*)	1.090	0.004	—	11.3
			$(^2A_1, C_{2v})^d$	CH(t)	1.091	0.004	—	24.9
				CH(c)	1.101	0.014	—	85.8
				CH(t*)	1.084	−0.002	—	−0.7
			$(^2B_1, C_{2v})^d$	CH(t)	1.095	0.008	—	32.1
				CH(c)	1.168	0.081	—	174.0
				CH(t*)	1.088	0.002	—	10.2
			$(^2A\cdot, C_s)^d$	CH(t)	1.084	−0.003	—	−2.8
				CH(t)·	1.114	0.027	—	81.5
				CH(c)	1.161	0.074	—	279.4
				CH(c)	1.083	−0.004	—	−7.6
cyclo-C_3H_6 **4**	CH	1.076	*cyclo*-$C_3H_6^{\cdot+}$	CH·	1.074	−0.002	−12.5	−12.3
$(D_{3h})^a$			$(C_{2v})^e$	CH	1.078	0.002	21.0	16.5

[a] See Ref. 9. [b] See Refs. 3, 4, and 13. [c] See Refs. 5 and 14. [d] See Refs. 6 and 14. [e] See Refs. 7, 8, and 15.

The a^H_{iso} constants considered are characterized by IHFC with terminal protons H* localized in the plane of carbon atoms (see Scheme 1). As known, the a^H_{iso} values depend on both the form of the matrix and the temperature of the sample, and the differences reach 7 and 3 Oe, respectively. The selected data that provide the maximum uniformity in three distinguished regions in Fig. 2 are presented in Table 2. The a^H_{iso} values for the other conditions can be found in the previously published works.[14,16–19] A smooth run of the curve is observed in all experiments, because the dependence of a^H_{iso} on n for RC of n-alkanes obtained, first, under different conditions and, second, with the restriction of $n \geq 2$ was analyzed. As can be seen from Fig. 2, constant a^H_{iso} (250 Oe) for $n = 0$ (RC of a hydrogen molecule, $H_2^{\cdot+}$) lies on the same line (*1*) as experimentally established values of a^H_{iso} for $n = 2$ to 4. At the same time, the a^H_{iso} value (121.7 Oe) for $n = 1$ (RC of methane, $CH_4^{\cdot+}$ (C_{2v})) determined by the ESR method deviates strongly from dependence *1*.

Table 2. IHFC constants with protons H* in RC of n-alkanes $[H^*(CH_2)_nH^*]^{\cdot+}$

n	$a^{H^*}_{iso}$/Oe	Matrix	T/K	References
0	250*	—	—	—
1	121.7	Ne	4	13
2	152.5	SF_6	4	14
3	98.0	SF_6	4	14
4	61.5	SF_6	77	16
5	49.5	SF_6	77	16
6	41.0	$CFCl_2CF_2Cl$	77	17
7	30.0	$CFCl_2CF_2Cl$	77	17
8	22.0	$CFCl_2CF_2Cl$	77	17
9	17.0	$CFCl_2CF_2Cl$	77	17
10	16.0	$CFCl_2CF_2Cl$	77	17

* Estimation for $H_2^{\cdot+}$ based on a^H_{iso} = 508 Oe for H.[11]

However, this high deviation of a^H_{iso} (~200 Oe) for $n = 1$ can be eliminated, if correlations (4) and (5) are valid and the geometry of RC $CH_4^{\cdot+}$ in terms of MP2/6—31 G** corresponds to symmetry C_s rather than C_{2v}. Compared to the CH_4 molecule,[9] RC $CH_4^{\cdot+}$ of symmetry C_s [4] (see Scheme 1) contains three nonequivalent chemical bonds that are longer by 1.145 − 1.084 = 0.061 Å (1 H), 1.090 − 1.084 = 0.006 Å (1 H), and 1.108 − 1.084 = 0.024 Å (2 H). According to Eq. (4), these increments of the C—H bond lengths correspond to three values of IHFC constants: 200.1, 19.7, and 78.7 Oe, respectively (see Fig. 2).

Each of three indicated values of a^H_{iso} of RC $CH_4^{\cdot+}$ (C_s) falls sufficiently well on the corresponding curves (*1*)—(*3*) (see Fig. 2), which likely reflect three known[11] mechanisms of the appearance of spin density ρ on protons H* in σ-electronic RC of hydrogen, methane, and n-alkanes ($[H^*(CH_2)_nH^*]^{\cdot+}$). At $n = 0$ to 4 the contribution of one-electron spin delocalization (ρ^0) unambiguously predominates, and the essence of the other two mechanisms is in spin polarization (ρ^{sp}) and exchange spin polarization (ρ^{ep}).[11] Three contributions

indicated ($\rho = \rho^0 + \rho^{sp} + \rho^{ep}$) can easily be estimated, for example, in terms of the CNDO/SP scheme.[15,20]

It is noteworthy that Eq. (4) covers two ranges of a^H_{iso} values: negative (due to the predomination of the contribution of exchange spin polarization ρ^{ep} to spin density ρ on protons) and positive values (due to the predomination of delocalized spin component ρ^0). It is likely that Eq. (5) is related to the third mechanism of the spin density distribution in free radicals.[11]

When the a^H_{iso} constants of two protons localized in the symmetry plane of RC $CH_4^{\cdot+}$ of C_s symmetry are averaged, *i.e.*, C_{2v} symmetry is assumed, we obtain the value of (200.1 + 19.7)/2 = 109.9 Oe, close to that experimentally established (121.7 Oe) for RC of bideuteromethane $CH_2D_2^{\cdot+}$. Therefore, it can be supposed that RC $CH_4^{\cdot+}$ of C_s symmetry is really present in the neon matrix at 4 K, and the dynamic equilibrium of two C_s-symmetric forms of RC (dynamic Jahn—Teller effect) results in the semblance that RC $CH_4^{\cdot+}$ has a higher C_{2v} symmetry.

This assumption is favored by the data for RC $C_3H_8^{\cdot+}$, which in the $CFCl_2CF_2Cl$ matrix (unlike the SF_6 matrix) contains the central fragment CH_2, whose electronic configuration resembles that of RC $CH_2D_2^{\cdot+}$ (*cf.* state $^2B_1$ with symmetry C_{2v} and state ^2A with symmetry C_s in Table 1). The experimental value a^H_{iso} = 100 to 110 Oe is considerably closer to the value theoretically averaged for the C_s-structure of $C_3H_8^{\cdot+}$ ((279.4 — 7.6)/2 = 135.9 Oe) calculated (174 Oe) for the C_{2v} form (state $^2B_1$ of RC in Table 1). According to the calculations,[6] for $C_3H_8^{\cdot+}$ with reduced symmetry, the ^2A state (C_s) is less favorable by only 0.3 kcal mol^{-1} than the higher-symmetric $^2B_1$ state (C_{2v}). Taking into account the aforesaid, it cannot be excluded that under the conditions of low-temperature matrix isolation the C_s conformation of $CH_2D_2^{\cdot+}$ and, hence, $CH_4^{\cdot+}$ becomes somewhat more stable than the C_{2v} structure. The resemblance of electronic configurations of CH_2 fragments and close values of a^H_{iso} for methylene protons in RC $CH_2D_2^{\cdot+}$ (121.7 Oe) and $CH_2Me_2^{\cdot+}$ (100 to 110 Oe) confirm the known fact that the D atom and CH_3 group are equally weak electron donors compared to the H atom.[21]

In Fig. 2, IHFC constants a^H_{iso} for $n \geq 9$ correspond to the line parallel to the x axis. This is related to the fact that the unsolved singlet appears in the ESR spectra of RC of *n*-alkanes at $n \geq 11$ instead of the triplet typical of n = 2 to 10, which does not allow one to obtain IHFC constants from the spectra.[17] Nevertheless, according to the ESR data,[18] the a^H_{iso} value for n = 12 is almost the same as for n = 10, while these values are only approximately twofold lower for n = 16 and 34. Since the slope of the line is apparently small (see Fig. 2, line *3*), it is accepted conventionally to be equal to zero. The almost unchanged adsorption maximum in the Raman spectra of *n*-alkanes with n = 12 to 30 in $CFCl_3$ and CCl_4 studied for n = 4 to 30 (see Ref. 22) indirectly justify these assumptions.

It is important to mention other two areas of application of the dependence of a^H_{iso} on Δ(C—H) (see Fig. 1). First, absolute values $|a^H_{iso}| \leq 30$ Oe correspond to increments $|\Delta(C—H)| \leq 0.01$ Å. Therefore, the use of C—H bond lengths of initial molecules that are almost unchanged upon ionization is justified for comparative quantum chemical calculations of electronic properties of hydrocarbon RC with such values of a^H_{iso}. By the contrary, considerable lengthening ($\Delta(C—H) \geq 0.02$ Å) of chemical C—H bonds upon ionization of hydrocarbons should be taken into account for σ-electronic RC with typical $a^H_{iso} \geq 50$ Oe (by Eqs. (4) and (5)).

As a rule, adiabatic ionization of hydrocarbon compounds results in lengthening of the $C(sp^3)$—H bonds, for which $a^H_{iso} > 0$ in RC formed. At the same time, the $C(sp^2)$—H bonds of ionized molecules usually shorten and become corresponding to $a^H_{iso} < 0$. When the proton has no spin density, the bond length of the corresponding chemical C—H bond remains nearly unchanged upon ionization.

All changes in chemical bond lengths and bond angles in similar fragments of molecules and RC are mutually matched.[2] Therefore, fragments of hydrocarbon RC with negligible spin densities on protons should have almost the same geometry as initial and single-type neutral molecules. Taking into account the aforesaid, we can simplify considerably quantum chemical analysis of radiospectroscopic and other physicochemical parameters of complex paramagnetic compounds.[1,2,11]

Second, the dependence presented in Fig. 1 makes it possible to substantiate geometrically the widely used empirical rule, according to which deprotonation of hydrocarbon RC in the ion-molecular process occurs by elimination of the proton possessing the highest spin density.[14] In fact, the higher the positive a^H_{iso} constant (in the range of Δ(C—H) up to 0.08 Å), the longer and weaker the C—H bond and, hence, the easier it can be broken. According to the accepted opinion,[14,16,23] even the moderate (~30 Oe) difference in constants a^H_{iso} of hydrocarbon RC can serve as an indicator of selective elimination of the proton, on which the positive spin density is higher.

Special emphasizing of the positive sign (β) of the spin density (and, hence, a^H_{iso}) is very substantial, because, as the regularity established testifies (see Fig. 1), negative (α) values correspond to shortening and, hence, strengthening of C—H bonds in hydrocarbon RC. Even if the absolute value of IHFC constant a^H_{iso}, that characterizes such a bond is maximum, the breakage of this bond followed by elimination of H^+ (channel of deprotonation of RC) is not facilitated and after shortening becomes most difficult due to strengthening of the bond. Therefore, efficiency of ion-molecular processes of other types increases noticeably.[24]

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