

Mechanisms of decomposition of hydrocarbons in electrical discharges

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Abstract - The mechanisms of decomposition of hydrocarbons in electric discharge plasmas are discussed, with special reference to: (i) plasma parameter measurements, (ii) composition of stable and unstable chemically active particles, (iii) mechanisms of ionization, excitation and decomposition including solid polymeric products generated by nonequilibrium chemical kinetics.

INTRODUCTION

Much work has been published on the study of the decomposition of hydrocarbons in nonequilibrium electrical discharges in which gaseous and solid polymeric products are generated, e.g. linear and cyclic saturated and unsaturated hydrocarbons and aromatic compounds. The dependence of outputs in stable products on external discharge parameters — such as pressure, gas-flow rate and electric power — have been used in the past to elucidate mechanisms of chemical reactions. The method using small accepting admixtures, applied successfully in the past for studying reactions in photo- and radiation chemistry, have not been so successful in the case of plasmas because (i) they may give a large variation of internal plasma parameters; and (ii) known radical or ion acceptors may have the opposite effect due to decomposition, ionization or excitation. Analogy of plasmachemical product composition with photochemical, radiochemical or mass-spectrometrical ones was used in interpretation also. But this way is not informative because of large variation of product composition with plasma parameters and complexity of chemical conversations with participation of electrons, radicals, excited particles and negative and positive ions.

Chemical reactions in nonequilibrium cold plasmas are initiated, as a rule, by collisions of molecules with electrons having large energy taken from electrical field immediately. Many particles having large chemical activity are generated by electron molecule collisions such as electronically and vibrationally excited molecules, negative and positive ions and radicals (ref. 1). Simultaneously some stable products may be generated. All particles may take part in following collisions with electrons, molecules, and one with another, giving secondary reactions. Heavy particles energy is low if the gas temperature is low. But by large specific power of discharge it may be large enough to give thermal pyrolysis reaction (Fig. 1,2). In addition, due to electron-molecule primary collisions hot atoms and radicals may be generated which are very active in chemical reactions even at low gas temperature.

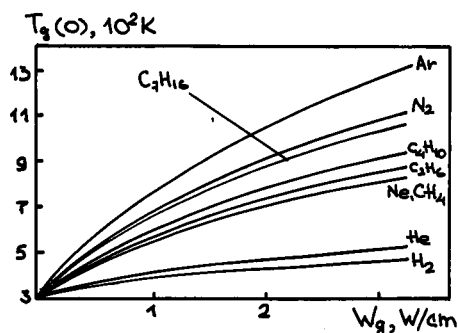


Fig. 1. Gas temperatures on the axis of discharge through some gases in tubular reactor versus specific power at $T_g(R) = 300$ K.

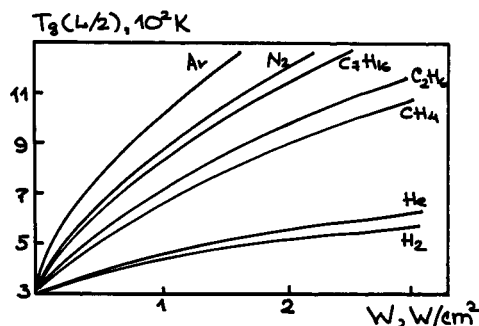


Fig. 2. Gas temperatures at the middle line between parallel plate electrodes in diode type reactor versus specific power with $L=2$ cm, $R \gg L$ at electrodes $T = T_g(0) = T_g(L) = 300$ K.

Due to this reason the chemical reaction mechanism in nonequilibrium plasma may be very complex and dependent on internal plasma parameter range. It is necessary to note that determination of active particles, giving main contribution in product generation is difficult because of the various type of active particles there are in any electrical discharges through any gases but not all of them are important in chemistry. Hence it is necessary for the plasmachemical reaction study to use the method of choice of most probable mechanisms of chemical reactions and physical processes in nonequilibrium plasmas (ref. 1). The method is based on the quantitative study of generation and decay kinetics of any particles in the frame of nonequilibrium chemical kinetic theory (ref. 2). To realize the method in practice is desirable to have measurements of all internal plasma parameters which influence the direction and rate of the chemical reactions (Table 1).

TABLE 1. Discharge parameters and internal plasma parameters which are necessary to know for mechanisms studying in nonequilibrium plasmas

Parameters	Measuring technique
<u>Discharge parameters :</u>	
Power , W , W	Electrotechnical devices
Electrical current, I, mA	
Electrical field strength, E, V/cm	Probes
Gas pressure, p, Pa	Membrane or capacitive manometers
Gas flow rate, G, cm ³ /s	Volume gas flow meter
<u>Internal plasma parameters</u>	
<u>Energy of particles :</u>	
Electron energy distribution function (EEDF), $f_e(E_e)$	Electrical probes, optical spectroscopy
Heavy particle (gas) temperature, T_g , K	Thermoprobes, thermocouples, Doppler broadening of spectral lines
Rotational temperature of molecules , T_{rot} , K	Optical spectroscopy, laser included, Raman spectroscopy
Vibrational temperature or distribution function of vibrational level populations	
<u>Particle densities :</u>	
Electrons , n_e	Electrical probes, absorption or reflection of microwave radiation, Stark broadening of spectral lines ($n_e \cdot 10^{13} \text{cm}^{-3}$)
Ions , n_i	Mass-spectrometry
Excited particles, n_i^*	Optical spectroscopy
Radicals, n_r	Optical spectroscopy, mass-spectrometry, ECR-spectrometry in gas phase, with matrix isolation on surfaces, radical trapping with ECR
Stable reagents and products	Chromatography, mass-spectrometry, Chromatomass-spectrometry, IR -absorption, laser induced fluorescent
Total heavy particle density, N_0	Calculation from measured pressure and gas temperature

Review of the works concerning hydrocarbon chemical reactions under discharge conditions shows insufficient knowledge of plasma parameters. In many cases even external parameters, such as specific electric power, are not reported. Investigations were carried out using various reactor constructions and discharge types - direct current, high frequency and microwave discharges. Without internal plasma parameters having been measured it is difficult to compare the results of various workers and to make objective conclusions about mechanisms of chemical reactions.

More detailed studies were performed using direct current discharge through mixtures of rare gases with methane and C₅-C₇ - hydrocarbons (ref. 3-15). The internal plasma parameters, radical and stable product compositions were measured. Variation of hydrocarbon contents and discharge current makes it possible to study kinetic order of reactions. Important results were obtained by means of labeled isotopic techniques which allow to discriminate the products of primary decay from products of the secondary one.

This lecture is based on the results of plasma parameter measurements and composition of stable and unstable chemically active particles. Mechanisms of ionization, excitation and hydrocarbon decomposition are discussed including generation of gaseous and solid polymeric products by means of nonequilibrium chemical kinetics.

PLASMA PARAMETERS, IONIZATION AND EXCITATION MECHANISMS

Plasma parameters are best studied in positive column of direct current glow discharges through rare gases (ref. 1). But addition of small concentrations of hydrocarbons to rare gases gives large variation of electric field strength, mean electron energy and density (Fig. 3). Most sharp variations are observed at additions of $\alpha = 0,01-0,05\%$ C-C₆H₁₂. At further increases of α from 0,05 to 2%, the variations are smaller and plasma parameters are nearly constant in this range. Decreasing the electrical field strength results in hydrocarbons having ionization potential lower than excitation potential of the rare gas metastable atomic levels. When the electric field strength is increased (ref. 1,3,4,6) the result is opposite. In more typical former case, gas temperature is lowered due to high heat transfer coefficient of hydrogen generated as a decomposition product and due to the decrease in electric field and specific power. To reduce electric field, E/N_0 is decreased as a result. Addition of hydrocarbons to rare gases decreases fast electron density even if E/N_0 is constant (ref. 8-10). Both effects decrease coefficients of processes initiated by electron impacts and electron drift velocity. Electron density is increased to compensate decrease of drift velocity and to maintain constant electric current.

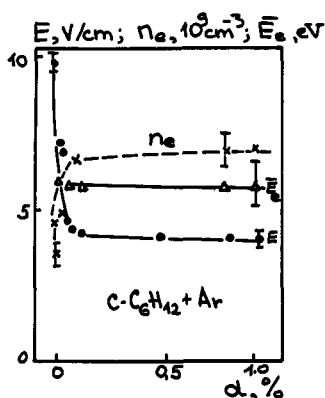


Fig.3. Effect of addition of small concentrations of hydrocarbons to rare gases in d.c. glow discharges — on electric field strength, mean electron energy and density.

Ionization rate must increase to give larger electron density in spite of decrease of electric field. Therefore, ionization mechanisms by hydrocarbon addition are varied. Ionization proceeds in glow discharge through pure rare gas under sufficient high current density ($j > 1 \text{ mA/cm}^2$) by a stepwise path: excitation of metastable atomic levels by electron impacts followed by ionization of metastable atoms by second electron impacts (ref. 1,6). Metastable levels excitation rate is decreased due to hydrocarbon addition and metastable atom densities are lowered due to decrease of density of fast electrons and quenching by hydrocarbon molecules. At very small additions ($\alpha \neq 0,001\%$) quenching is low compared to the electron impact (<5%). However, the electric field strength is already decreased (Fig. 3). It is connected with contribution of Penning ionization occurring by collisions of metastable rare atoms with hydrocarbon molecules. The greater the hydrocarbon addition, the larger is molecular quenching and when $\alpha = 1\%$ its rate is at hundred times larger than quenching of metastables by electrons. Metastable densities are at hundred times less than the ones in rare gases. As a result the rates of stepwise processes of ionization and upper atomic levels excitation are decreased. This effect gives observable quenching of luminosity of discharge when hydrocarbons are added.

On addition of cyclohexane to argon more than 0,01% main ionization process is Penning ionization having efficiency which is equal to $0,56 \pm 0,3$ per collision. Direct ionization of hydrocarbon molecules by electron impact gives contribution only at larger additions.

The process is main in pure hydrocarbon discharges where the electric field strength is increased again. The reason of this increase is deficiency of fast electrons in its energy distribution which is the more the more are additions.

If the ionization potential of hydrocarbons is larger than excitation energy of rare gas metastable level (for example, methane has $E_{ion} = 12,5$ eV, and argon $E_m = 11,55$ eV) electric field strength is increased by small extent because of decrease of stepwise ionization due to quenching of metastable atoms which is not compensated by appearance of new ionization channel (ref. 1,15).

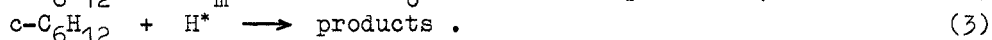
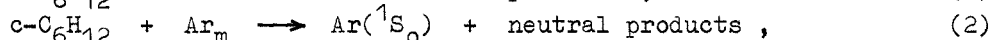
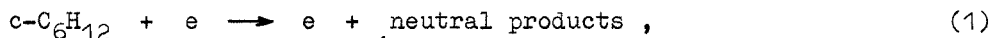
Penning ionization was used in (ref. 11) to explain the slow changing of electric field with time in discharge through mixtures of Ar, He and Ne with benzene ($\phi = 0,1\%$). But characteristic time of the variation was equal to ten seconds which is much more than the survival time of metastable atoms varying from 10^{-3} s in pure rare gases to 10^{-5} s in mixtures. Hence this explanation is not correct. It is more probable that slow variations of electric field as observed are forced by chemical reactions, occurring particularly at reactor walls.

Small variation of plasma parameters in mixtures of rare gases with 0,1-2% hydrocarbons allow to study kinetic order of reaction depending on hydrocarbon concentrations. Independence of plasma parameters on gas residence time in discharge ($\tau > 10^{-3}$ s) gives possibility to carry out kinetic studying with simple interpretation. Influence of by - electrode regions on the chemical reactions was excluded by freezing of products in by - electrode zones (ref. 5-7).

MECHANISMS OF DISSOCIATION OF HYDROCARBONS

Dissociation rates of cyclohexane as measured are increased according to linear - low with increase of hydrocarbon concentration in mixture with argon, increased monotonically depending on current density and gas pressure and independent of gas residence time in discharge within error limits (Fig. 4). This independence allow to exclude the reverse reaction of cyclohexane generation from dissociation products. This conclusion was confirmed by experiments with use of mixtures of protonated and deuterated cyclohexanes (1:1 and 1:10) in argon. In this case products do not contain isotopic mixed cyclohexanes.

It was shown by evaluation of reaction rates of all energetically possible reactions that the main contribution in cyclohexane dissociation may give collisions with electrons, metastable argon atoms and hot hydrogen atoms :



Hot hydrogen atoms (H^*) may be generated due to primary dissociation processes (1,2) via decay of highly electronically excited molecules of cyclohexane. Hot atoms dissipate their energy during collisions with argon atoms be-

fore collision with hydrocarbon molecules (3). Hence reaction probability depends on hydrocarbon concentration in mixture. Upper limit of reaction (3) rate can not be more than rate of hot atoms generation in reactions (1,2), because in every act of reaction (3) hot atom must disappear. Therefore contribution of reaction (3) can in better case only enlarge the dissociation rate by factor two. It is the case if the every act of reactions (1,2) gives appearance of hot atom and every hot atom gives disappearance of cyclohexane molecule in reaction (3). But really contribution of this reaction in hydrocarbon dissociation evidently is not so large because the dissociation rate is directly proportional to cyclohexane concentration in mixtures as observed (Fig. 4^a).

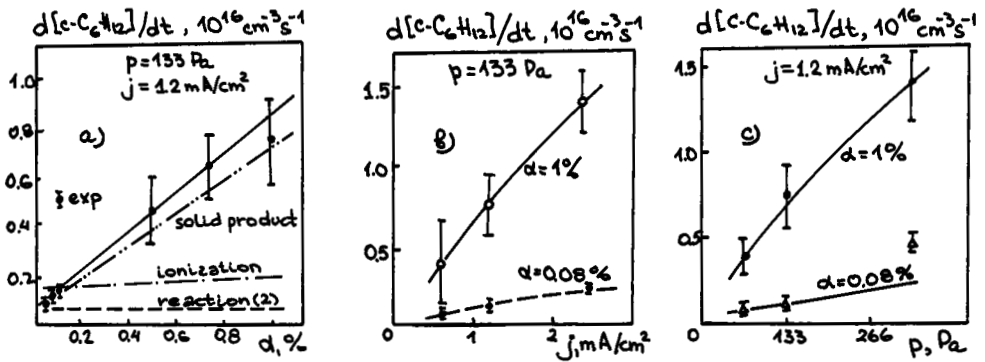
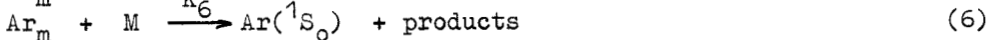
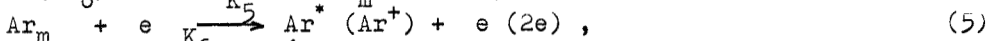


Fig. 4. Dissociation rates of cyclohexane versus its addition to argon in mixture (a), discharge current density (b) and gas pressure (c) with $R=0,5 \text{ cm}$; $G=390 \text{ cm}^3/\text{s}$. Lines are relative dependences calculated: 1 - due to reaction 1, 2 - 2; 3 - ionization rate of cyclohexane due to collisions with argon metastable atoms; 4 - rate of solid products generation determined from C -atom balance. Points are dissociation rate measured

Taking into account the excitation and deexcitation of metastable argon atoms



the reaction (2) rate equals

$$j_2 = \frac{K_2 [C-C_6H_{12}] K_4 \cdot n_e [Ar]}{K_6 [M] + K_5 n_e} = \frac{j_D K_4 \cdot n_e [Ar]}{1 + K_5 n_e / K_6 [M]} \quad (7)$$

In expression (7) probability of dissociation due to molecular quenching (2, 6) is introduced

$$j_D = K_2 / K_6 \quad (8)$$

Also it is taken into account that molecular quenching is large compared with rare atom one, and cyclohexane dissociation degree is small. Then using the rate coefficients values $K_5=(4,5 \pm 1,5) \cdot 10^{-17} \text{ cm}^3 \text{ s}^{-1}$; $K_6=10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (ref. 13,14) and $\alpha \approx 0,5\%$ (α is relative concentration of cyclohexane in initial mixture) it can be shown that reaction (2) rate is not dependent on α as ratio $K_5 n_e / K_6 [C-C_6H_{12}] = 5 \cdot 10^3 \alpha \approx 0,1$ and electron density and energy are constant in the range $0,1\% \leq \alpha \leq 2\%$ (Fig. 3). Rate of the reaction (3) must be

directly proportional to α . As follows from data of Fig. 4, reaction (3) gives main contribution in the range $0,1\% \leq \alpha \leq 2\%$. The reaction (2) contribution is significant only if $\alpha \leq 0,1\%$.

The same dissociation rates were observed for other C_5 - C_7 hydrocarbons under same conditions (Table 2). Reduced electric field is the same too for various hydrocarbons excluding benzene. Hence possibility of Penning-ionization by collisions of metastable argon atoms with the hydrocarbons is nearly constant. For benzene value of E/N_0 is enlarged, which connected with diminishing of Penning-ionization probability due to appearance of additional channels such as intermolecular conversion of excitation energy.

TABLE 2. Steps and rates of decomposition of number hydrocarbons in glow discharge through their mixtures with argon under the same conditions: $j=2,4$ mA/cm²; $p=133$ Pa; $\alpha_{C_xH_y} = 1\%$; $d_{tube} = 1$ cm (ref. 4,5)

Hydrocarbon	Degree of dissociation, %	Residence time, t , 10^{-3} s	Dissociation rate, $cm^{-3}s^{-1}$	Reduced electric field, E/N_0 , $10^{-16}V \cdot cm^2$
c-C ₆ H ₁₂	15 \pm 2	3,4	14 \pm 2	1,2
c-C ₅ H ₁₀	12 \pm 2	4,2	9,0 \pm 1,4	1,2
c-C ₆ H ₁₁ CH ₃	7 \pm 3	3,4	6,5 \pm 2,6	1,1
C ₆ H ₁₄	10 \pm 2	4,5	7,1 \pm 1,3	1,2
C ₆ H ₆	12 \pm 2	4,2	9,0 \pm 1,4	1,7

The small variation of dissociation rates mean the approximate equality of dissociation cross-sections under electron - hydrocarbon collisions. This conclusion is confirmed by calculation of cross - sections of dissociation via excitation of optically allowed electronic transitions by electron - molecular impacts (Fig. 5) (ref. 15). The dissociation rates as calculated using this cross - section and electron energy distribution as calculated for pure argon plasmas (ref. 10) are significantly lower than measured ones (Fig. 6). This discrepancy may be explained by contribution of excitation of optically inallowed electronic transitions which is main process for the hydrocarbons as was shown in the past for the methane, ethane, propane and butane (ref. 16). The same dissociation mechanism including stage (1-3) was observed for mixture of methane with rare gases (ref. 6).

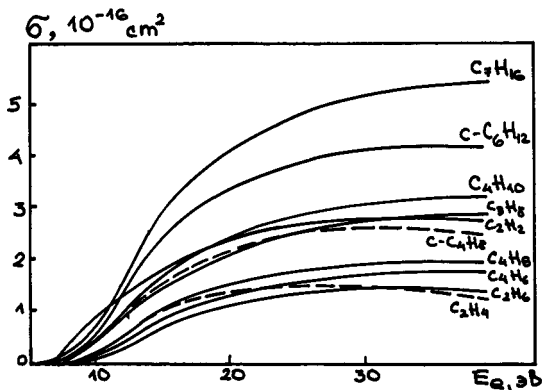


Fig. 5. Cross sections of hydrocarbons dissociation by electron impacts followed by excitation of optically allowed electronic transitions

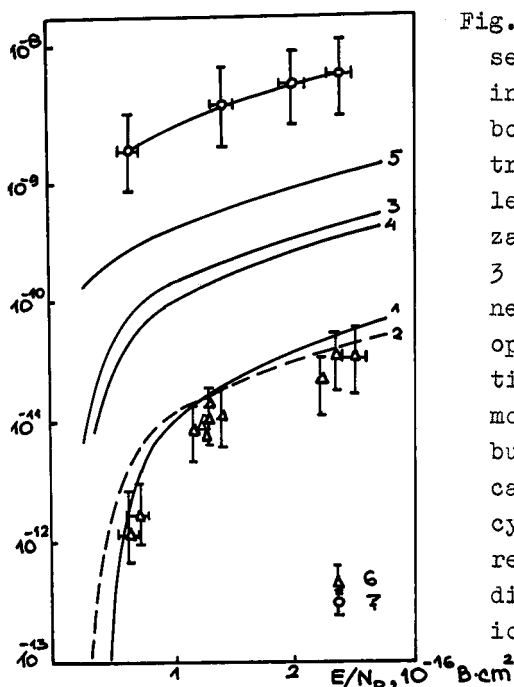


Fig. 6. Rate coefficients of processes initiated by electron impacts in mixtures of argon with hydrocarbons ($\alpha < 10\%$) versus reduced electric field. 1 - argon atom metastable level excitation; 2 - direct ionization of cyclohexane molecules; 3 - direct dissociation of cyclohexane molecules through excitation of optically allowed electronic transitions; 4 - the same as (3) for butane molecules; 5 - direct dissociation of butane through excitation of optically electronic transitions; 6 - cyclohexane dissociation rate measured; 7 - ionization rate measured in discharge and determined by Penning ionization of cyclohexane

Thus initiation of hydrocarbons decomposition under nonequilibrium plasma conditions in mixtures with rare gases is due to collision of molecules with fast electrons and excited metastable rare atoms. Direct dissociation by electron impacts gives main contribution beginning from small additives (a few tenth of percent) up to 100% hydrocarbons. Radicals generated due to primary decay do not cause chain processes at low gas temperatures ($T_g = 500-600$ K). The dissociation rate can be twice due to influence of hot atoms and radicals generated during primary decay. The same dissociation mechanisms must be observed for hydrocarbons in other types of discharges such as HF and MW under the same range of parameters: $\bar{E}_e \approx 1,5-2$ eV; $x_e = n_e/N_0 < 10^{-5}$; $T_g < 600$ K.

Variation of dissociation mechanism is possible due to enlarged gas heating at high specific discharge power (Fig. 1,2), when the radical reactions may give chains. In (ref. 17) it was supposed that increasing dissociation rates of number hydrocarbons as observed was caused by contribution of reactions with participation of vibrationally excited molecules without discussion of gas heating effects. This supposition seems to be impossible because of high efficiency of hydrocarbon vibrational relaxation (ref. 18).

MECHANISMS OF GENERATION OF STABLE GASEOUS PRODUCTS

Solid polymeric films are the main product of C_4-C_6 hydrocarbon decomposition in direct current discharge through mixtures of argon with hydrocarbons. The films are deposited on the reactor walls, electrodes and samples inserted to plasma (Table 3). Gaseous products composition of $c-C_6H_{12}$ dissociation in mixture with argon is nearly the same that one in pure $c-C_6H_{12}$ (Table 4, columns 2,3). But change of discharge type from dc to HF and MW discharge through methylcyclohexane gives variation of gaseous product composition and ratio of outputs of gaseous and solid products (Table 4, columns 8-10).

TABLE 3. Outputs of gaseous and solid products of hydrocarbons decomposition in discharges through mixtures with argon (ref.4,5)

Hydrocarbon	$\alpha_{C_xH_y}, \%$	Discharge	Sum of gaseous products	Sum of solid products
c-C ₆ H ₁₂	100	Constant current glow, p=133 Pa	-	observed
c-C ₆ H ₁₂	1,0	- " -	12	88
c-C ₅ H ₁₀	1,0	- " -	14	86
C ₆ H ₁₄	1,0	- " -	38	62
C ₆ H ₆	1,0	- " -	9	91
C ₄ H ₁₀	1,0	- " -	-	observed
c-C ₆ H ₁₁ CH ₃	1,0	- " -	29	71
c-C ₆ H ₁₁ CH ₃	100	High frequency (HF)	79	21
c-C ₆ H ₁₁ CH ₃	100	Microwave (MW)	93	7

TABLE 4. Main stable products of number hydrocarbons decomposition in electrical discharges (sum of gaseous product without hydrogen is equal to 100%)

Stable product	Constant current glow discharge, p=133 Pa					HF-dis-charge	MW-dis-charge	
	c-C ₆ H ₁₂ $\alpha=100\%$	c-C ₅ H ₁₀ $\alpha=1\%$	C ₆ H ₁₄ $\alpha=1\%$	C ₆ H ₆ $\alpha=10\%$	C ₄ H ₁₀ $\alpha=1\%$	c-C ₆ H ₁₁ CH ₃ $\alpha=1\%$	c-C ₆ H ₁₁ CH ₃ $\alpha=100\%$	c-C ₆ H ₁₁ CH ₃ $\alpha=100\%$
CH ₄	1,0	-	-	-	31,8	-	1,4	3,9
C ₂ H ₆	6,7	7,5	5,7	20,0	-	8,1	13,0	4,5
CH ₂ =CH ₂	28,3	39,0	31,3	16,6	2,9	28,3	25,5	15,0
CH≡CH	22,8	18,1	21,7	16,3	44,1	16,3	19,1	2,7
C ₃ H ₈	3,5	2,4	4,5	15,8	-	-	3,1	2,0
CH ₃ CH=CH ₂	7,9	7,2	18,4	10,1	-	9,3	13,3	-
CH≡CCH ₃	1,6	1,4	3,9	-	2,2	2,4	1,5	-
C ₄ H ₁₀	-	0,7	-	7,0	-	-	-	-
C ₃ H ₆ =CH ₂	2,4	1,9	-	1,1	-	2,1	2,5	-
C ₂ H ₄ =C ₂ H ₄	1,2	1,4	-	0,8	1,7	-	-	-
CH ₂ =(CH) ₂ =CH ₂	7,9	7,5	-	-	-	1,5	5,9	0,3
C ₅ H ₁₂	-	-	-	1,4	-	-	-	-
c-C ₅ H ₁₀	-	-	-	-	-	-	-	-
C ₂ H ₄ =(CH)=CH ₂	2,0	0,1	2,1	-	-	-	-	-
c-C ₅ H ₈ =CH ₂	0,4	0,8	1,0	-	-	-	-	-
C ₆ H ₆	0,8	1,1	-	-	-	-	-	0,4
c-C ₆ H ₁₁ CH ₃	2,8	3,1	-	-	-	-	-	-
c-C ₆ H ₉ CH ₃	-	-	-	-	-	-	59,0	48,5
c-C ₆ H ₁₀	9,8	8,6	-	-	10,0	-	-	3,4
c-C ₆ H ₁₂	-	-	-	-	25,2	-	5,6	3,4
c-C ₆ H ₈	2,0	0,1	-	-	-	-	-	-
Other	-	-	4,8	13,3	4,0	16,3	17,3	-
			(C ₈ ;C ₆)	(C ₅ ;C ₆)	(C ₇ ;C ₉)	(C ₅ -C ₉)	(C ₅ -C ₉)	

Gaseous products are main in HF and MW discharges (Table 3). Products generated due to breaking off C-C bonds predominate among the gaseous products in dc discharges. At that time products generated due to breaking off C-H bonds predominate among the decomposition products in HF and MW discharges, where more parts of products are gaseous ones. In earlier works (ref. 7) it had been supposed that gaseous products were generated mainly due to decay of cyclohexane rings preferably to stable molecular fragments of $C_2:C_2:C_2$; $C_3:C_3$ and $C_2:C_4$ types.

But it is clear that decay can give radicals which being unstable particles give rise to stable products as result of secondary reactions.

Determination of radicals in discharge plasmas is one of the more complex problems in studying dissociation mechanisms (Table 1).

In earlier works radicals were identified by means of optical spectra of plasmas. But this method gives certain identification as rules only for atoms and two atomic radicals and in exclusive cases for 3-atomic radicals (ref.19) In the cases of manyatomic radicals the identification is difficult due to diffusion of spectra and hence is based on chemical proof only. It gives uncertain conclusions about type of radiating radical (Table 5). Mass-spectroscopic technique gives a certain information in the case of light hydrocarbons (C_1, C_2), but for heavier ones difficulties of identification are very large.

Spin trapping technique was found to be the most effective one for heavy hydrocarbons. A number of substances (such as 2-methyl-2-nitrozopropane, nitrobenzene, phenyl-thret-butyl nitron etc) exposed to plasma can capture the radicals giving stable substances (so-called adduct-radicals) with characteristic ESR-spectra, depending on type of radicals. Exposing of spin trapping to plasma of discharge in pure argon gives no ESR-signals. In latter case surface of spin trapping positioned at 5 cm distance from discharge in gas flow is bombarded by excited and charged particles which flow is much more than in mixture of argon with hydrocarbons. Therefore only hydrocarbon radicals give ESR-signal (Fig. 7). Information on type of radicals is derived from pick to pick distance and pick intensities in ESR-spectra of adduct-radicals. The view of adduct-radical ESR-spectra is different from ESR-spectra of the free radicals.

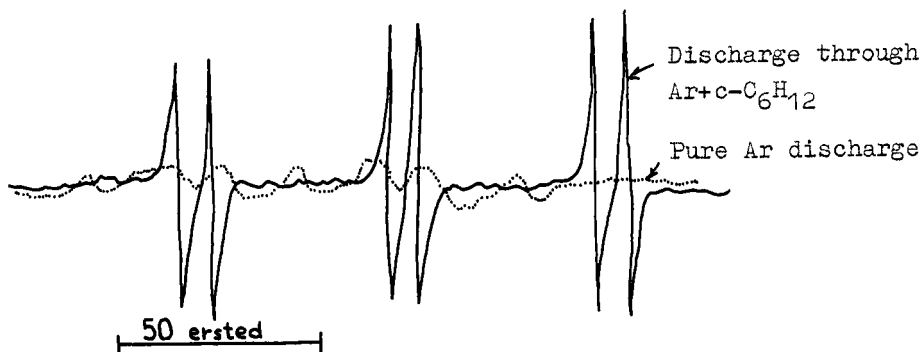


Fig. 7. ESR-spectra of adduct-radicals observed after exposition of radical trapping to discharge through mixture of C_6H_{12} with argon and pure argon

TABLE 5. Main radicals*), observed in nonequilibrium electric discharges through hydrocarbons

Hydrocarbon	Observed radicals	Measuring technique	Conditions	Reference
CH ₄	CH ₃ , CH ₂ , C ₂ H ₃ , C ₂ H ₅ , H	Mass-spectrometry	HF-discharge, p=13-133 Pa	(ref.20)
CH ₄	H, CH, CH ₂ , C ₂ , C ₃	Optical spectroscopy	Impuls discharge	(ref.19)
	H		Constant current glow discharge	(ref.6)
C ₆ H ₆	C ₆ H ₅ (?)	Optical spectroscopy	Constant current glow discharge through mixture of helium with 1-5% hydrocarbons	
C ₆ H ₅ CH ₃	or		p=26-200 Pa ;	
C ₆ H ₅ C ₂ H ₇	C ₆ H ₅ CH ₂ (?)		j=1-2 mA/cm ²	(ref.21)
C ₆ H ₅ CH ₂ C ₆ H ₅				
C ₆ H ₅ (CH ₂) ₂ C ₆ H ₅				
C ₆ H ₆	H, CH, C ₂ , C ₂ H (or C ₄ H ₂ ⁺)	Optical spectroscopy	HF and MW-discharges , p=26-266 Pa ; W = 15-100 W	(ref.22)
	C ₆ H ₅ CH ₂ (?), C ₆ H ₅ C(?)			
	C ₆ H ₄ (?), C ₆ H ₅ CH ₂ (?)			
C ₆ H ₆	C ₆ H ₅	Radical trapping	HF-discharge	(ref.23)
C ₆ H ₅ CH ₃	C ₆ H ₅ CH ₂			
c-C ₆ H ₁₂	H, c-C ₆ H ₁₁	Radical trapping	Constant current glow discharge through mixture of argon with hydrocarbon	
c-C ₅ H ₁₀	H, c-C ₅ H ₉			
c-C ₆ H ₁₁ CH ₃	H, CH ₃ , c-C ₆ H ₁₁ CH ₂ , c-C ₆ H ₁₁ , c-C ₆ H ₁₀ CH ₃			
C ₆ H ₁₄	C ₆ H ₁₃ , H			
C ₆ H ₆	C ₆ H ₅ , H		α=1%; p=133 Pa ; j=1, 2 mA/cm ²	(ref.4, 12, 15)
C ₄ H ₁₀	C ₄ H ₉	Radical trapping	Silent discharge	(ref.24)
C ₅ H ₁₂	(C ₂ H ₅) ₂ CH			
C ₆ H ₁₄	C ₆ H ₁₃			
c-C ₆ H ₁₂	c-C ₆ H ₁₁			
C ₇ H ₁₆	C ₇ H ₁₅			
C ₆ H ₅ CH ₃	C ₆ H ₅ CH ₂			

*) Concentrations of any other radicals are less than 20% of ones shown in the table .

It was shown by spin trapping technique that the main hydrocarbon radicals generated during decomposition are the products of breaking off hydrogen atom from rings, chains or methyl substitution group (Table 5). In the case of HF and MW discharges in benzeneproducts, their fragmentation were observed (ref. 22). But this fact is accounted for high specific discharge power (Fig. 1,2) followed by high gas temperature and high rate of secondary reactions. The latter are responsible for the appearance of C₂-C₃-radicals in the case of methane (Table 5). Quantitative data concerning radical concentrations are

absent because all known techniques are nonquantitative and give only relative concentration.

Analyses of data of tables (3-5) show that among gaseous products are a few which can be generated from radicals (Table 5). At first view it could be to confirm the conclusions of ref. 7 about molecular break-up of cyclohexane rings.

To clear up this question and to study mechanism of chemical reactions special experiments were carried out with dc discharge by using isotope-labeled technique. The mixtures of protonated and deuterated cyclohexanes in ratios 9:1 and 1:1 with total concentration of 1% were introduced to argon and used as working gas in dc discharge. Products were analysed by chromatomass-spectrometry (ref. 4,15).

The gaseous products were shown to divide in relation with its isotopic composition to three groups.

The first group consisted of products, containing only hydrogen or only deuterium atoms: ethene (C_2H_4 ; C_2D_4); acetylene (C_2H_2 ; C_2D_2); methylenecyclopentane ($c-C_5H_8=CH_2$; $c-C_5D_8=CD_2$); cyclohexene ($c-C_6H_{10}$; $c-C_6D_{10}$); 1,3 and 1,4 cyclohexadienes ($c-C_6H_8$; $c-C_6D_8$); benzene (C_6H_6 ; C_6D_6).

The second group consisted of products having comparable output all partially substituted proto-deutero compounds: ethane and propane (Table 6).

TABLE 6. Isotopic abundance of cyclohexane decomposition products included in 2^d and 3^d group, see text: $\alpha=1\%$; $j=2,4$ mA/cm²; $p=133$ Pa. Sum of registered isotopic abundance of every product is equal to 100%. Isotopic composition of initial mixture $c-C_6H_{12}:c-C_6D_{12}=B:1$

Product	Isotop	Abundance, %		Product	Isotop	Abundance, %	
		B=1	B=9			B=1	B=9
Ethane	C_2D_6	12	5	Butene-1 (Butene-2 numbers in bra- ckets)	C_4D_8	16 (32)	2(4)
	C_2D_5H	18	7		C_4D_7H	22 (19)	7(5)
	$C_2D_4H_2$	28	22		$C_4D_6H_2$	4 (1)	4(3)
	$C_2D_3H_3$	42	66		$C_4D_5H_3$	4 (2)	2(6)
Propane				$C_4D_4H_4$	5 (0)	0(1)	
	C_3D_8	12	1	$C_4D_3H_5$	5 (0)	4(0)	
	C_3D_7H	13	4	$C_4D_2H_6$	5 (1)	4(2)	
	$C_3D_6H_2$	9	7	C_4DH_7	17 (21)	22(10)	
	$C_3D_5H_3$	12	12	C_4H_8	22 (24)	55(75)	
	$C_3D_4H_4$	8	8	Methyl- cyclo- hexane	$c-C_6D_{11}CD_3$	24	24
	$C_3D_3H_5$	14	10		$c-C_6D_{11}CD_2H$	8	3
	$C_3D_2H_6$	15	22		$c-C_6D_{11}CDH_2$	9	6
C_3DH_7	17	36	$c-C_6D_{11}CH_3$		10	18	
Propene				$c-C_6H_{11}CD_3$	11	2	
	C_3D_6	51	32	$c-C_6H_{11}CD_2H$	12	5	
	C_3D_5H	44	51	$c-C_6H_{11}CDH_2$	11	6	
	$C_3D_4H_2$	0	11	$c-C_6H_{11}CH_3$	15	37	
	$C_3D_3H_3$	5	6				

The third group consisted of products having unequal isotope outputs: methylcyclohexane, propylene and butene (Table 6). Direct primary decay of cyclohexane can give only products of the group. Relative output of various products of this group depends on initial hydrocarbon concentration in mixture, current density and gas pressure (Fig. 8 a,b,c).

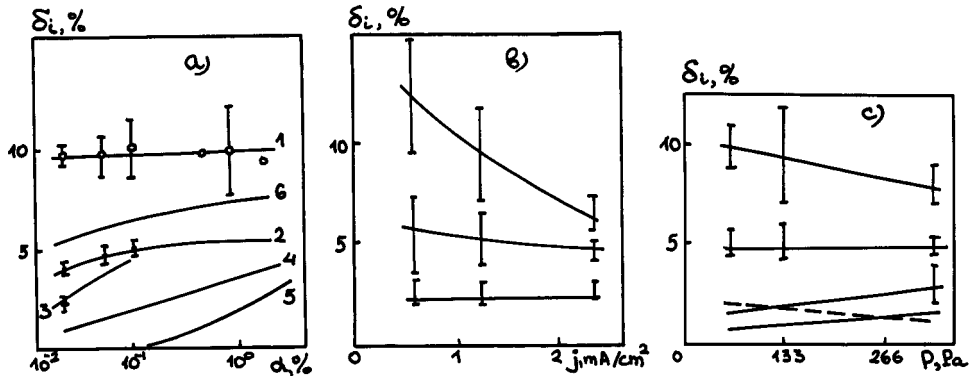


Fig. 8. Outputs of some stable products related to quantity of decomposed cyclohexane molecules as a functions of initial hydrocarbon concentration in mixture with argon (a), discharge current density (b) and gas pressure (c); a) $p=133$ Pa; $j=1,2$ mA/cm²; 1 - C₂H₄; 2 - C₂H₂; 3 - c-C₆H₁₀(2,3)*); c-C₆H₈=CH₂(23); c-C₆H₈-1,3 (76); c-C₆H₈-1,4(60); C₆H₆(3,3); C₃H₄(12); 4 - C₂H₆(1,5); C₃H₈(1,75) C₃H₆(1,8); 5 - c-C₆H₁₁CH₃(20); C₄H₁₀(220); 6 - C₄H₈-1(14); C₄H₈-2 (20); C₄H₆-1,3(31); b) $p=133$ Pa; $\alpha=1\%$; 1 - C₂H₄; C₂H₆(3,7); C₃H₈ (12,5); C₃H₆(5); C₄H₈-1(16); C₄H₈-2(12); 2 - C₂H₂; C₃H₄(14,2); c-C₆H₁₁CH₃(6,5); c-C₆H₁₀(3); c-C₆H₈=CH₂(12); C₆H₆(10); C₄H₆-1,3; c) $j=1,2$ mA/cm²; $\alpha=1\%$; 1 - C₂H₄; C₂H₂(1,6); C₃H₆(25); 2 - c-C₆H₁₀; c-C₆H₈(14); C₆H₆(10); C₂H₆(9); 3 - C₄H₄-1,2(7); C₄H₈-2(8,8); C₄H₆-1,3; 4 - C₅H₈=CH₂(10); 5 - c-C₆H₄CH₃. *) Factors by which must be divided the figure values to obtain the true values are given in brackets

A number of them could be generated by means of consecutive dehydrogenation of primary products during their collisions with hydrogen atoms and electrons. In these cases their relative output could be increased by increasing current density because of increase of concentration of atomic hydrogen and electrons. But relative products outputs of first group were decreased or invariable as observed with current density increases (Fig. 8b). This fact excludes significant contributions of consecutive dehydrogenation reactions. The same is true about other reactions of dehydrogenation by collisions with other radicals as generated in primary decay. In both cases relative outputs of these products must be increased with α . Indeed some increase of output was observed for C₂H₂, c-C₆H₁₀, c-C₆H₈ and C₅H₈=CH₂ in the range of small α (Fig. 8a) and with increase of pressure (Fig. 8c). But this dependence must be more sharp in the case of consecutive reactions, namely $\delta_i \sim \alpha^2$ and $\delta_i \sim p^2$. Weak dependence of relative outputs on α , p and current density exclude entirely contribution of consecutive dehydrogenation. Therefore all products of first group are direct products of primary decay of excited cyclohexane molecules by electron impacts (1,2). Dependence of

various product outputs on discharge parameters and λ is accounted for different path of excitation. By small λ collisions of cyclohexane with metastable argon atoms (reaction 2) give significant contribution, but by larger λ ($\lambda \geq 0,1\%$) impacts of electrons give main contribution. Appearance potentials of various products are different as the decay takes place from various levels followed by variation of products composition with electron energy.

Then primary decay of excited cyclohexane takes place according to the scheme : breaking of C-H bonds

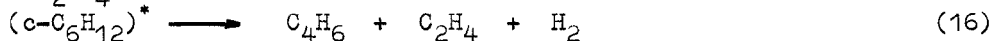


Strong isotopic effect was observed for benzene. Its output due to decay of $c-C_6D_{12}$ was at times higher than in the case of $c-C_6H_{12}$. This can be explained by strong influence of mass on the complex decay (12).

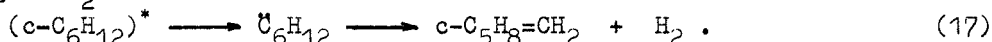
Breaking of C-C bonds of types $C_2:C_2:C_2$:



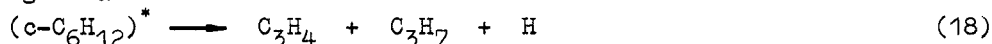
and types $C_2:C_4$



and breaking off one C-C bond followed by isomerization of biradical and escaping of H_2



The first group of products includes possibly an allen. Its isotopic composition was not studied. But dependence of allen output on discharge parameters is the same as observed for products of first group (Fig. 8a,b,c). Hence it is generated due to reaction



which is only one example of ring distribution of types $C_3:C_3$ with appearance of stable products. Decay of type $C:C_5$ was not observed.

Reaction scheme (9-18) differs significantly from supposed earlier (7), according to which main decay reactions give saturated alkanes directly (ethane, propane, butane). Isotopic abundance of alkanes with nearly equal outputs of all protonated-deuterated products as observed (Table 5) is the proof of generation of these alkanes during secondary reactions most possibly with participation of radicals.

Generation of radicals can occur during primary decay of excited molecules:

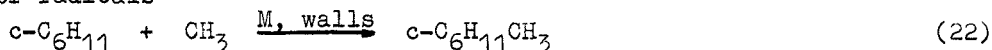


Direct experiments confirmed possible appearance of stable products and radicals with simultaneous escaping of several hydrogen atoms and molecules and simultaneous breaking off several C-C and C-H bonds by direct impact of electrons with molecules. For example, following products were observed as result of butane dissociation: $CH_2(13, 5 \pm 1)$; $CH_3(9, 0 \pm 0, 5)$; $CH_4(11, 0 \pm 0, 5)$; $C_2H_2(13, 0 \pm 1, 0)$; $C_2H_3(13, 0 \pm 1, 0)$; $C_2H_5(10, 5 \pm 1, 0)$; $C_3H_3(14, 0 \pm 2, 0)$; $C_3H_4(14, 0 \pm 2, 0)$; $C_3H_5(12, 5 \pm 1, 0)$; $C_4H_2(15, 0 \pm 1, 0)$; $C_4H_3(14, 0 \pm 1, 0)$; $C_4H_4(14, 5-1, 0)$; C_4H_5

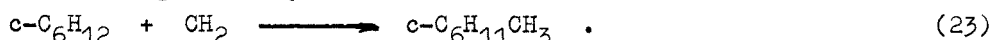
(12,0[±]2,0); C₄H₆(12,0[±]1,0). Appearance potentials as measured are shown in brackets (ref. 25).

The products of the third group are generated as result of secondary reactions of primary decay products. Their unsubstituted parts are products of primary decay. They are connected with radicals, generated in primary decay and/or in secondary reactions.

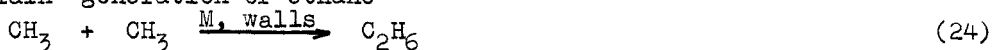
Methylcyclohexane is one of most interesting products of this group. It has entirely protonated or entirely deuterated ring connected with methyl group and output of products with all partly deuterated and protonated methyl groups are nearly equal (Table 6). Hence it can be generated by two paths: recombination of radicals



or due to including of methylene radicals to C-H - bond



In the latter case c-C₆H₁₁CH₂D; c-C₆D₁₁CH₂D and c-C₆D₁₁CD₂H must not be observed. It is contrary to data (Table 6). Hence the reaction (23) gives no contribution and generation is due to recombination of radicals (22). Methyl radicals must be nearly equally deuterated - protonated. Such radicals can explain generation of ethane

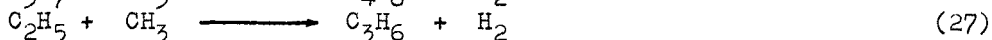
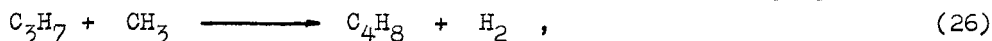


and propane also



with their isotopic composition (Table 6).

Butenes and propylene are generated most probably due to disproportion reactions



and radical recombination



These stable products of ring breaking are C₂:C₂:C₂ type (C₂H₄, C₂H₂), one C-C bond (C₅H₈=CH₂) and breaking of several C-H bonds (C₆H₁₀, C₆H₈, C₆H₆) are generated during primary decay of excited cyclohexane molecules. The ring breaking of C₄:C₂ (C₄H₆) and C₃:C₃ (C₃H₄) types makes a small contribution. Total output of gaseous stable products due to direct breaking of C-C bonds is less than 7,5% and of C-H bonds is less 2,5%. Output of gaseous products generated due to secondary reaction, with participation of cyclohexyl radical (main radical in plasma) namely methylcyclohexane is less than 0,4%.

Outputs of gaseous products of recombination of other radicals are one order value larger in spite of the other radicals concentrations as measured are at 5 times less than cyclohexyl one. This allows to suppose that cyclohexyl radicals take part in building of solid products on the walls.

MECHANISMS OF DEPOSITION OF FILMS

The solid polymeric film is the main product of decomposition of all studied hydrocarbons in dc discharge (Table 3). Rate of film deposition increases proportionally to cyclohexane concentration in initial mixtures under condition of constancy of all other plasma parameters including the charged particle flow to surface. Hence deposition does not occur due to put into film of cyclohexane ions being the main ions in plasma at $d > 0,1\%$. To study con-

tribution in deposition of unsaturated hydrocarbons generated due to hydrocarbon decomposition a number of experiments were carried out — the mixtures of deuterated cyclohexane and protonated ethene were used by total concentration of hydrocarbons in argon equals 1%. Deposited films do not contain the hydrogen if ethene addition was equal to one generated due to decomposition of cyclohexane in mixture with argon (Table 3). The hydrogen was observed in films only by increasing the ethene concentration in mixture to ten times (3% C_2H_4 + 1% $c-C_6D_{12}$ + 96% Ar) (ref. 4,5,15). Hence the unsaturated in plasma do not give significant contribution to film deposition.

The most probable mechanism of film deposition as studied contains building in of heavy radicals generated due to breaking of C-H bonds. Building up is due to recombination with free bonds on surface generated due to its bombardment by energetic plasma particles. The latter gives rise to further destruction of bonded radicals, atomic hydrogen and light radical desorption (CH_2 , CH_3 ...). Free bonds generated as a result recombine one with another giving generation of cross links and double bonds, and with radicals coming from plasma giving films growth.

Recombination with hydrogen atoms leads to decay of free bonds. This reactions explain mixed isotopic composition of light radicals in plasma, because hydrogen is main gaseous product of hydrocarbons decomposition.

Such a mechanism is confirmed by data observed using benzene. In this case film contained aromatic structures — phenyl, bi- and three- phenyl fragments. Concentrations of the latter were diminished with increasing bombardment intensity by means of decreasing of benzene concentration in initial mixture, or additional treatment grewed films by pure argon plasma.

Main role was shown in free bonds generation to play ions by using mixture of methane with rare gases. Ion building in films is not significant as substitution of hydrocarbon ions by xenon ones do not influence the rate of film growth (ref. 13,26). Hence growth is due to hydrocarbon radicals. Cyclohexyl radicals built into film in cyclohexane being main products of primary decomposition and give rise to very low outputs of gaseous products.

CONCLUSION

This application of quantitative method to studying of chemical reaction mechanism in nonequilibrium plasma diagnostic (ref. 1) allow to find most probable paths of gaseous and solid products generation during decomposition of hydrocarbons in dc discharge plasma (ref. 4,5,15). The mechanism differs significantly from those proposed earlier (ref. 7,21,22 etc).

The main difference shown here is that primary decay gives rise to radicals even in the reactions generating stable products too. Most decays are due to break of C-H bonds followed by solid film deposition as result of radical recombination on surfaces. Breaking of C-C bonds gives rise to gaseous products. Primary decomposition reactions are decays of electronically excited hydrocarbon molecules. Excitation is made by collisions with electrons and meta-stable atoms.

Role of ions in decomposition reactions is negligible. They play large role in solid product deposition rate and composition due to bombardment of surfaces.

The mechanism is valid in glow discharges by low pressures ($p < 500$ Pa) and current densities ($j < 10$ mA/cm²). Under other conditions for example in discharges with higher specific power and pressure particularly in HF and MW discharges a new detailed analyses is needed based on the quantitative diagnostics of plasma.

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