COMPREHENSIVE STUDY OF REACTION KINETICS OF SIMPLEST UNSATURATED FLUOROCARBONS IN NON-EQUILIBRIUM PLASMA. MECHANISMS OF GAS PHASE TRANSFORMATIONS.

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Abstract

Chemical kinetics of simple unsaturated fluorocarbons in RF gas discharge have been systematically studied and generalized in a range of kinetic residence times from 1 ms under the pressure of 0.2-0.4 Torr typical for a gas discharge polymerization. The solid data on the composition of fluorocarbon discharge plasmas of C2F4, C3F6, c-C4F8 have been obtained in for C1-C8 products firstly. A mechanism of chemical transformations has been derived and computer simulated to disclose the role of undetectable low density highly reactive products. All studied monomers follow the first order decomposition kinetics with the reaction constants of about (6÷15) s^{-1} (power density ~0.2 W/cm^3). The gas phase chemistry is controlled by free radical reactions. Main reactions leading the gas phase synthesis are as follows: mutual recombination of monoradicals, reactions of monoradicals with carben CF2, and reactions of atomic fluorine with unsaturated molecules. Chain reactions are of little consequence. C4-C6 free radicals are practically the only source of carbon in surface film formation under the typical gas discharge polymerization condition.

INTRODUCTION

Optical methods (emission and adsorption) and mass-spectroscopy were extensively used to study the gas phase composition of electric discharges in simplest saturated fluorocarbons. The results accomplished by the data derived from the beam experiments provided a view on the mechanism of chemical reactions. Those methods, however, are not so much informative in case of plasmas having more complicated chemical composition like the discharges in unsaturated fluorocarbons. That is why not only the reaction kinetics but even the gas phase composition of such discharges was not known, and hence, understood. Optical methods by themselves can give a precise identification but for only a few particles. In contrast, a mass-spectrometry detects practically any product but never distinguish them in a complex mixture.

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A gas chromatography (GC), being the well known method of gas phase analysis of stable products in chemistry, has shown a great promise for a kinetic analysis of gas discharge transformations of hydrocarbons [1] and fluorocarbons [2] solving two fundamental problems. It can provide: 1) the best correspondence of the detected (measured) stable products to the real composition of the gas probe sampled from the object; 2) a maximum entirety of the analysis, that is a maximum number of quantitatively measured components concurrently. GC has no competitors in these two principal points and can be accomplished by mass-spectroscopic and optical (IR) identification.

As for the validity of model gas kinetic mechanisms, their justification depends exclusively on the entirety of the gas phase analysis. The only kinetic set of a majority of the numerous stable gas phase products gives mathematically approved basis for a modeling. Specially measured selected unstable highly reactive components never approve complicated mechanisms and never substitute that basis. The correlations of such products with the rates of target plasma processes is accompanied by the uncontrollable variations of other products and parameters. Consequently, the observation of only some highly reactive components provides either more or less important "checkpoints", sometimes just misleading arguments, but never can be considered as a correct basis of modeling.

Here, we describe an approach to the kinetic study and the reaction mechanism of simplest unsaturated fluorocarbons derived from the comprehensive study of non-equilibrium plasmas of an RF capacitively coupled discharge under the well defined kinetic conditions. The conclusions presented here are valid for any other discharge system in the range of specific discharge and kinetic parameters.

KINETIC CONDITIONS and APPROACHES

Among numerous reactors utilizing glow type discharges there are only a few which are suitable for a kinetic analysis in terms of physical chemistry. Such reactors possess well defined gas dynamic characteristics along with a well defined distribution of physical parameters, main of which is the specific discharge power controlling a plasma density. It does not necessarily mean that other reactors are worse. Some of them found industrial applications, even those operating under the non-steady state conditions. Nevertheless, it can be definitely shown that those reactors are principally not suitable for the detailed studies of the reaction kinetic mechanisms.

It is well known that only two types of ideal chemical kinetic reactors exist: ideal mixing and ideal replacement or plug flow type. However, only the second one can be characterized as having the well defined residence time. The first one possess a wide distribution function of the gas residence time. Traditional cylindrical DC discharge tubes represent typical reactors capable for operating under the plug flow conditions. These objects should be the most beneficial for the studies of reaction mechanisms. However, they have two imperfections: 1) it is very difficult, if possible, to maintain a steady state DC discharge in electronegative gases; 2) initial chemical transformations proceed in the entrance plasma zone having indefinite boundary.

The box-type RF discharge reactor [2] meets the majority of experimental demands for the kinetic studies being the tubular rectangular shaped reactor accomplished

by the strictly limited gas entrance plasma boundary. **Fig. 1** shows a three dimentional time surface of the reactor which explains its characteristic features in case of continuos or pulse discharge operation. One can see the distribution of the kinetic residence time along the reactor length in case of a pulse (**t1, t2**) or a steady state operation ($t \geq t3$). The distribution of kinetic time is shown for a longitudinal points of the reactor depending on the discharge duration to show the evolution of surface kinetic conditions in a pulse discharge mode.

Pulse and continuos discharge operation can accomplish one another. However, in case of deposition or etching these modes of operation are not always interchangeable in respect to the surface. It depends on the characteristic times: whether the deposition or etching can be considered as proceeding under the constant conditions or not, is it dependent on the pulse duration or not. Without taking into consideration the above mentioned kinetic characteristics it is practically impossible to justify any kinetic statement.

Gas phase composition and gas discharge chemical transformations of simplest unsaturated fluorocarbons **C2F4, C3F6, c-C4F8** have been firstly systematically studied and generalized in a wide range of kinetic residence times of about **0.002-2 s** in continuous and pulse **RF** capacitively coupled discharge. The experimental data have been obtained under the well defined plasma and gas dynamic conditions under the gas pressure of about **0.2-0.4 Torr** typical for the gas discharge polymerization condition. The specific discharge power density was about **0.2-0.3 W/cm^3** under the excitation frequency of **40.68 MHz**, linear gas velocity up to **150 cm/s**, the gas flow cross-section **20 (h) x 60 (w) mm^2**. The foolproof method of kinetic gas chromatography supplemented with **IR** and chromato-mass-spectrometric identification of products was used. Optical emission spectroscopy, thermal, Langmuir and surface kinetic probes were utilized as complementary diagnostic tools.

GAS PHASE TRANSFORMATIONS

General observations

1) Fluorocarbons entering the plasma zone undergo the decomposition under an electron impact well described as a first order kinetics with the reaction constant of about **6.5, 15.8, 9.5 s^{-1}** for **C2F4, C3F6,** and **c-C4F8**, respectively. The decomposition rate was constant along the discharge thus justifying the longitudinal discharge uniformity. Initial decomposition of **c-C4F8** proceeds faster in the entrance cold plasma-surface sheath in comparison with **C2F4** and **C3F6** which do not show any feature. Pulse discharge was also used for 1-100 ms range. The condition of a quasi steady state discharge was supported up to the lowest limit of about **1-2 ms** discharge pulses in case the gas phase was completely refreshed before every pulse ($t_{off} > 0.1$ s).

2) The discharge residence time could be considered as a true kinetic parameter of similarity only at the gas velocities higher than about **50 cm/s**. Below this limit a longitudinal diffusion distorts the plug flow conditions leveling off the longitudinal distributions of products.

3) The gas phase composition of all studied discharges is similar. Some differences concern only for the ratio between the components. The kinetics of initial gas

phase synthesis is linear for practically all studied products. The main part of all products consists of C1-C4 components. The consequence of the product appearance proves the stepwise character of the processes and their high rate. All initial decomposition products, excluding free radicals, have been observed experimentally. For instance, C5-C6 products appear at times less then 10 ms in C2F4 discharge. The data obtained are proved to be suitable for a kinetic analysis.

4) The saturated fluorocarbons, main of which finally are CF4 and C2F6, keep the constant production rate for long residence times and monomer conversion deeper than 50 %, for CF4 even up to 90% monomer conversion.

5) All unsaturated products are intermediate and approach their maximum density at residence times of about 50-80 ms.

6) Atomic fluorine is generated in dissociation processes initiated by an electron impact with a reaction rate of about $(2^{+2}_{-1})\cdot 10^{16}$ $cm^{-3}\cdot c^{-1}$. It brings the considerable contribution to the gas phase synthesis through the generation of free radicals in reactions of fluorination of unsaturated molecules. Direct fluorination of C3F6 by atomic fluorine (without discharge) was studied as well in order to disclose the reaction mechanism of atomic fluorine and the set of cross recombination reactions between thus generated monoradicals. The rate of fluorine production in discharges is almost constant up to the monomer conversion of about 60-90 %. Atomic fluorine is efficiently consumed in the gas phase reactions with unsaturated products, and hence, practically does not play any role in surface processes. It never etch the film under the typical deposition conditions.

7) CF2 carben density is slightly varied along the gas flow and does not correlate with any of the gas phase products or the film deposition rate. The characteristic time of CF2 generation up to the steady state level is about 10-20 ms. CF2 density drops down in about 30 ms when the RF power is stopped.

8) No one detected gas phase product correlates with the film growth rate.

9) The neutral gas phase chemistry strongly controls the film deposition rate and structure under the condition of uniform plasma parameters.

Modeling and conclusion

The set of experimental data gives a very clear qualitative picture of the gas phase transformations of fluorocarbons. For a quantitative treatment the chemical kinetics was described as a set of physical-chemical processes and reactions and computer simulated.

The following approaches and assumptions have been applied:

1) Main variable parameters of modeling have been the reaction constants of initial decomposition of fluorocarbons for the reaction routes which could not be discriminated experimentally.

2) The decomposition of initial products was not included in the modeling since the rates of their production exceed the decomposition on orders of magnitude.

3) The reaction constants taken from literature and those derived from experimental estimations were not varied.

4) Since the dependence of the reaction constants of fluoroalkyl radicals on pressure are absent in literature, the high pressure limit was supposed. There are some doubts on the use of these constants for CF2 and CF3.

5) The recombination constants of fluoroalkyl radical have been selected from literature taking into consideration their ratio.
6) The recombination constants for radicals heavier that C4 have been assumed to be the same, since for C3-C4 radicals the recombination constant practically does not depend on the number of carbon atoms.
7) Recombination constants of fluoroalkenyl radical have been assumed in a similar way as those for fluoroalkyls.
8) Since the recombination of ethenyl radicals gives undetectable products, and perfluorbutin, which concentration was not measured in kinetic experiments, their densities were denoted as undetectable, and they were not included in the total mass balance.
9) The constants of radical cross recombination reactions have been calculated as: $k_{ij} = 2 \times \sqrt{(k_{ii} \times k_{jj})}$, which is a correct approximation for fluoroalkyl C1-C3 radicals. Here k_{ij} - cross recombination constant; k_{ii}, k_{jj} - mutual recombination constants.

A modeling was performed using the computer code "KINETICS" [3] to examine the validity of the whole model and discriminate the mechanism of heavy particle formation. The modeling was performed for 20-40 main chemical components involved in 50-100 chemical process depending on the monomer.

A good correspondence between calculated and experimental data has been found for all monomers. The main channel of heavy product formation is a set of recombination reactions of initial radicals and CF2. Atomic fluorine appears to be very efficient in generation of fluorocarbon radicals via the reactions with unsaturated molecules. Ion-molecular reactions seem not to play any role in C2F4 and c-C4F8 transformations and can only give a very small contribution in case of C3F6 discharge.

The kinetics of surface deposition is based on a contribution of neutral C4 and heavier radicals. Somewhat about 5-20 % contribution can be assigned to the surface contribution of stable C6-C8 products ("adsorption" mechanism). Light C1-C3 radicals can essentially contribute to the film growth only at the initial kinetic stages or other special condition when the density of heavier radicals is low, for example, under the etching or very low pressure conditions. Chain reactions of unsaturated molecules do not contribute appreciably neither in the gas phase nor in the surface synthesis. A simplified schema of C2F4 transformations is shown in Fig.2 as an example.

References

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2. G.K.Vinogradov, A.G.Timokhov, D.I.Slovetsky, *High Energy Chem.*, **25** (1991) 271.
3. L.S.Polak, M.Ya.Goldenberg, A.A. Levitsky. *Calculation Methods in Chemical Kinetics*, Moscow, Ed. Science, 1984, 279 pp. (in Russian).

Figures:

Fig. 1. 3-d kinetic time surface of a box-rype plug flow reactor.
Fig. 2. Principal routes of chemical transformations of C2F4 in a gas discharge.

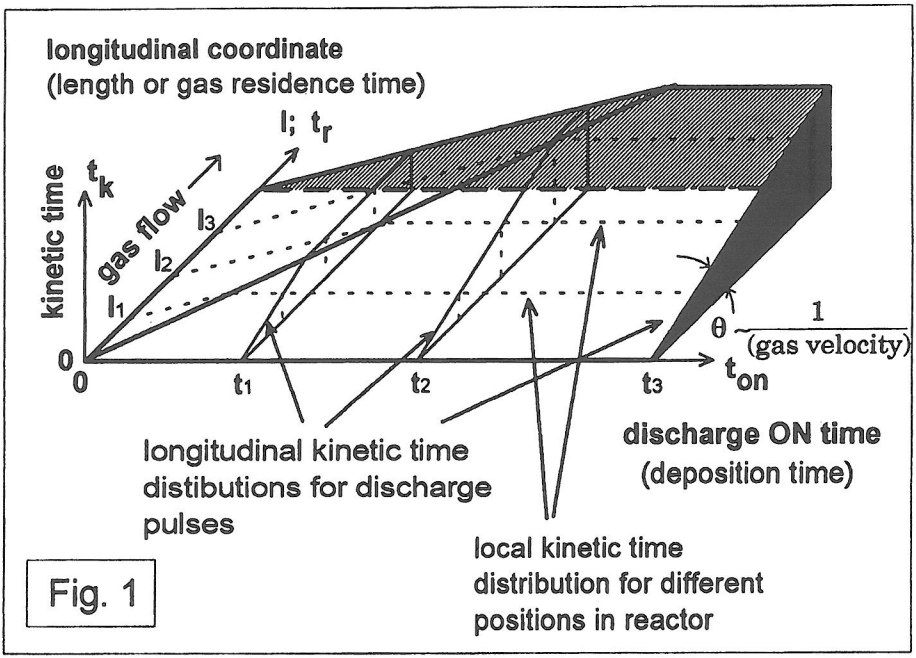
longitudinal coordinate
(length or gas residence time)
l; t_r
kinetic time
t_k
gas flow
l_3
l_2
l_1
0
0
t_1
t_2
t_3
t_{on}
θ
1
(gas velocity)
longitudinal kinetic time
distibutions for discharge
pulses
discharge ON time
(deposition time)
local kinetic time
distribution for different
positions in reactor

Fig. 1

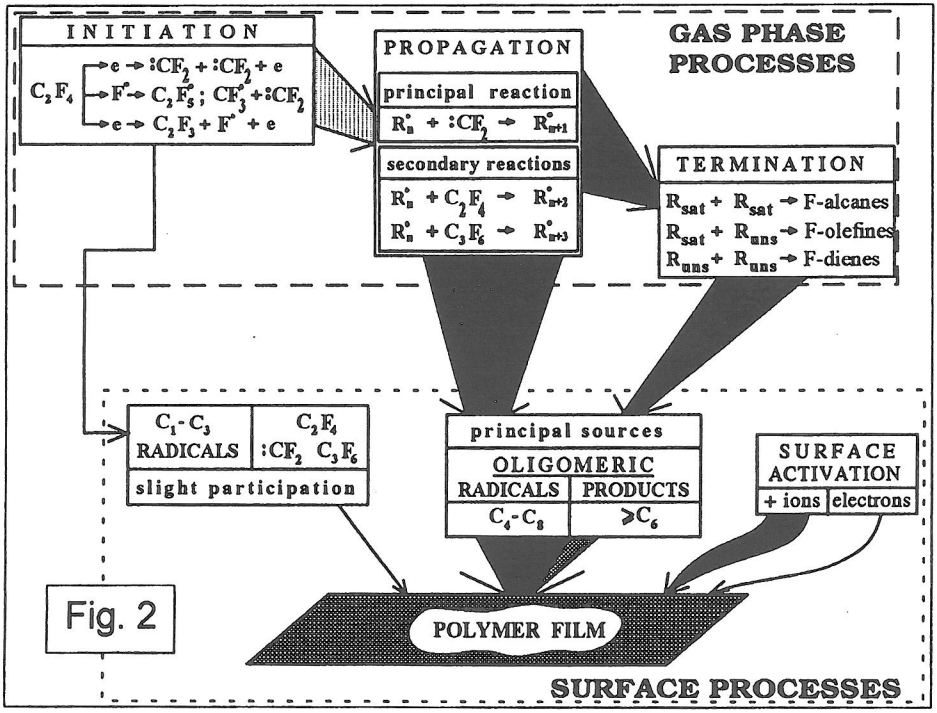
INITIATION
C_2F_4
e → :CF_2 + :CF_2 + e
F· → $C_2F_5^·$; $CF_3^·$ + :CF_2
e → C_2F_3 + $F^·$ + e
PROPAGATION
principal reaction
$R_n^·$ + :CF_2 → $R_{n+1}^·$
secondary reactions
$R_n^·$ + C_2F_4 → $R_{n+2}^·$
$R_n^·$ + C_3F_6 → $R_{n+3}^·$
GAS PHASE
PROCESSES
TERMINATION
R_{sat} + R_{sat} → F-alcanes
R_{sat} + R_{uns} → F-olefines
R_{uns} + R_{uns} → F-dienes
C_1-C_3
RADICALS
C_2F_4
:CF_2 C_3F_6
slight participation
principal sources
OLIGOMERIC
RADICALS
PRODUCTS
C_4-C_8
≥C_6
SURFACE
ACTIVATION
+ ions
electrons
POLYMER FILM
SURFACE PROCESSES

Fig. 2