The influence of the different elements of an organic molecule structure on the main kinetic parameters of its unimolecular reaction in the high-pressure region

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ABSTRACT

The most general dynamic tendencies of the energy redistribution in the high-pressure region are considered. Their influence on the possible deviations from the kinetic conceptions, which is now generally accepted, is examined. In this way, the structural elements of an organic molecule that promote internal energy mobilization in the high-pressure region and, conversely, hamper it, are defined. The first of these elements reduces both the Arrhenius parameters of the unimolecular reactions while the second leads to the opposite results. Some well-known exceptions to existing kinetic theories, which find an explanation in the framework of these proposed concepts, is considered. The proposed concept is very general as distinct from the existing dynamic studies, which investigate more particular details of the separate bond behaviors. The proposed general concept can broaden the study of chemical kinetics.

1. INTRODUCTION

The present paper is devoted to the dynamics of energy mobilization inside an energized molecule in order that a reaction will proceed in the high-pressure region. Presently, the dynamics picture of the energy flow in chemical kinetics is studied practically exclusively by the method of collision-induced relaxation of a vibrationally excited molecule, which has been the subject of continuing interest for the past several decades [1-6]. The problem of the internal energy mobilization of a molecule is studied mainly in the fall-off region, where it plays a decisive role and determines in particular the

transition in the high-pressure region. The existing dynamical method is concerned with the detailed treatment of molecular vibrations and the behavior of particular molecular coordinates as a function of time. Generally, this relaxation is studied during and after one collision.

In the present paper, in contrast to the existing dynamics method, an attempt was made to formulate those elements of the organic molecule structure that promote the concentration of the energy surplus of an energized molecule on the bond that is being broken or, conversely, that detain part of the energy on some structural group of bonds, disperse it between these bonds, and in this way impede energy concentration on the bond that is being broken. The first structural elements reduce the general energy quantity necessary for molecular activation (E), and also reduce the energy and the entropy of the transition state (A-factor) and the energy that remains on the reaction fragments. Note that in this case the negative transition state entropy, *i.e.*, negative entropy of activation, will be even in the simple bond fission reaction, which is absolutely impossible in the framework of the modern statistical Rice-Ramsperger-Kassel-Marcus (RRKM) theory. In so doing, energy activation also may be lower than the strength of the bond that is being broken. This is also impossible in the high-pressure region according to statistical theories, whereas in the fall-off region the usual well-known situation exists. Conversely, the second type of structural element leads to an increase in energy activation (E) and the pre-exponent (A-factor). In this case, the high A-factor and "loose" transition state may be even at its ringed form, when it has lost a few degrees of freedom. This is also impossible in the framework of the modern statistical theories.

This dynamic influence is contrary to the statistical one in many respects: the "loose" transition state means a lowering of the rate constant, and the rigid transition state means a rate increasing. The resultant of the both is more complicated than the statistical influence only. This is the real cause of many exceptions to the statisti-

cal RRKM theory (see below).

In the Introduction, both types of the above-mentioned molecular structures and some semi-empirical rules that result from them are outlined. In the subsequent parts of the article are discussed: the agreement between existing kinetic data and these semi-empirical rules; their limitations and the extent of their applicability; the connection between them and the existing dynamic method; and their ability to explain some known exceptions to modern statistical theories.

The main source of the existing kinetic data is, of course, the articles in the current kinetic literature. Other than this, a very comprehensive collection of rate data on thermally induced unimolecular, homogeneous gas phase reactions by Sydney Benson and O'Neal [7] should be noted, which unfortunately includes kinetic data only up to February 1968, and a fundamental book on unimolecular reaction by P. Robinson and K. Holbrook [8], which, in addition to kinetic theory, contains a significant collection of the experimental data.

The proposed method is not an alternative approach to the existing dynamical one, but rather a qualitative supplement, and a very general approximation. Nevertheless, it introduces a few new concepts that are very important for any branch of science, in that it aids our understanding and interpretation of experimental data, and confirms the direction that further research should take, particularly that using existing conventional methods. It is also important in that it explains the exceptions to existing kinetic theories. Probably existing dynamic methods and some others (particularly quantum scattering theory) will in the future incorporate this approach to study similar generalizations, and correct some of them.

We tried to cite the kinetic data of the usual static and flow method, which are intentionally obtained for the high pressure region only, and the data of the VLPP (shock tube technique) method only if they were obtained under strongly comparative conditions, since, in this case, the values of both the Arrhenius parameters are slightly dependent on the experimental condition.

The early kinetic data [7,8] were utilized only if their interpretation was not disproved in later works. We do not refer to the works in the field of quantum scattering theory, in particular the numerous works of the Miller Group (mostly published in the J. Chem. Phys.) in spite of many common ideas. These works, even for quantum mechanical transition state theory by the semi-classical method, represent a statistical but not a dynamical approach.

The general preconditions. When at its stretching a bond that is being broken falls into the region where the attraction between the atoms that it is forming is weakened (the anharmonic part of the potential curve), the neighbouring bonds are generally shortened as a result of a decrease in their resistance to this shortening. This liberates a part of their energy for the bond breaking. The shortening of the neighbouring bonds and the stretching of the broken bond mutually accelerate one another. A shift of the neighbouring bond atoms as a result of their shortening is further transferred along the molecular chains, which may participate in this manner in the internal energy mobilization of a molecule for the bond breaking.

A weak bond in the vicinity of stronger neighbouring bonds falls into its anharmonic region more often than they fall into theirs. It therefore uses part of their energy for stretching and breaking more often than conversely. This weak bond in such a surrounding is an acceptor of their common vibrational energy. Therefore, the breaking of a weak bond in such a surrounding increases the internal energy mobilization of a molecule. If the reaction takes place in the part of a molecule with stronger bonds, this reduces the rate of energy mobilization and promotes the energy dispersion, because the weak bond absorbs a part of their common energy.

The increase in the internal energy mobilization rate reduces the energy necessary for a molecule's activation and also the energy, and consequently the entropy, of the transition state, *i.e.*, it reduces both Arrhenius parameters: energy activation (E) and pre-exponent (A factor). The dispersion energy in a molecule leads to the opposite result: an increase in both Arrhenius parameters. The pre-exponent (A) is a more reliable indicator of these two processes than energy activation, because the latter is exposed to fewer influences of other factors. A surplus or lack of energy in the molecule produced as a result of these two contrary processes is taken away by reaction fragments with further relaxation.

The mobilization of the internal vibrational energy of a molecule in the high-pressure region is a purely kinetic effect, equally accelerating the direct and the back reaction. If the potential energy curve of the direct reaction has a back slope after the top, *i.e.*, the back reaction has energy activation and consequently an anharmonic region, it is accelerated in the same manner and to the same extent. The absence of the back slope decelerates both reactions (direct and back). Actually, in the absence of the back slope on the potential energy curve of the direct reaction, there is a high probability that, after achieving the barrier's top, the separated fragments will be captured back during the next vibration. The steeper the back slope, the lower is this probability. In such a manner, the internal energy mobilization of a molecule for bond fission in the high-pressure region, reducing both Arrhenius parameters, takes place in the most prominent form only when the remarkable activation

energy of the back reaction is available. This condition is, probably, not so critical for a ringed transition state. Here, the energy redistribution (inner relaxation) takes place inside a ring and the fragments moving off are, as a rule, neutral molecules but not radicals.

A less incisive example of internal energy mobilization is the case of a triatomic molecule whose bonds are both identical, but whose peripheral atoms have different masses. When the common vibration energy of two bonds approaches the detachment energy of one atom (E), the quicker light atom on average more often falls into the anharmonic region than does the heavy one, and therefore more often uses the energy of its bond than conversely. As a result, in opposition to statistical theories, the light atom has an additional advantage over the heavy one in the detachment energy, *i.e.*, it has less energy activation in spite of the identical potential energy threshold (E). The energy advantage can lead to a significantly greater difference between the reaction rates of the two isotopes (isotope effect) than only the difference in mass and velocity. Naturally, this advantage may be completely realized only at infrequent collisions of the triatomic molecule with surrounding particles (in the extreme case when there are no collisions at all), because these collisions destroy the dynamic interaction between two bonds and shift the bond breaking reaction in the region of the usual isotope effects.

The simplest example of the interaction of the two identical bonds, which is convenient for computer calculation, is represented by a hypothetical triatomic "molecule," restricted to a linear configuration and only two modes of linear vibration (no bending modes). The statistics of the light and heavy atoms' detachments from such a triatomic "molecule" has been studied at different surplus energies over a potential energy threshold [9]. For each energy surplus (ΔE), many vibrations are performed at the random initial conditions, in order to calculate the average parameters of the detachment separately for light and for heavy atoms. The interaction model and numerical procedure is usually accepted now for computer calculation of collision-induced vibration [1,4]. The "molecule" vibrates until one of two atoms, the heavy or the light one, detaches from the diatomic molecule remaining. The smaller the energy surplus (ΔE) is, the greater the prolongation of the vibration. Under such conditions, the ratio of the frequencies of light and heavy atom detachments significantly exceeds the known values of isotope effects. The light atom takes away on average a greater part of their surplus energy than the heavy one, *i.e.*, it makes better use of their common vibrational energy for its detachment. It can be said that light and heavy atoms compete with one another for a common energy excess and the possibility of

their detachment. The light atom, since its speed is greater (on average) than that of a heavy atom, benefits more frequently from this competition. These calculations have been performed in connection with the experimental discovery [9] of an anomalously large kinetic isotope effect for oxygen isotopes separation, which is also a motive for the present paper.

It is also necessary to consider the structural elements that impede the energy concentration on the bond that is being broken. As mentioned above, the significant difference in the parameters of the neighbouring bonds promotes the energy concentration on one of them and impedes the free passing of energy fluctuation along a carbon chain. The proximity of these parameters (in the extreme case, their full identicalness) must, conversely, promote the free circulation of the energy fluctuation in the system of these identical bonds, retarding its exit from this system to the bonds with other parameters. This proximity includes also the identicalness of the mutual locations of these bonds, *i.e.*, the symmetry of this bonds system. Such a system of similar or fully identical bonds is, to some extent, the energy fluctuation trap, detaining the energy fluctuation on its bonds and dispersing it between them.

As the branching of the carbon chain increases the number of identical bonds linked to one central atom, so also a ring having similar or fully identical bonds is representative of such a similar bonds fluctuation trap. In the first case of the branched chain the effectiveness of the energy dispersion (demobilization) has to increase in the row: primary, secondary, tertiary, quaternary (neopentane type) carbon atom. In addition, a carbon atom, in particular the other elements of the IV group of the periodic table, Si, Sn, Pb, may be in the center of the branching. In the second case of a ring that can include not only a carbon but also a heteroatom, the effectiveness of the demobilization process will be increased with more light movement of energy fluctuation inside the ring. This lightness depends on the proximity not only of the bonds' strengths but also of other parameters, first of all frequencies, masses of atoms, etc.

The case when the bond that is being broken is a part of the fluctuation trap corresponds to the most effective demobilization. When the bond that is being broken is not found in the fluctuation trap, the effectiveness of the demobilization depends on the structure and dimension of those parts of a molecule that are found between them. The more free energy circulating between these two parts of a molecule, the more the effectiveness of the demobilization increases.

Structural elements of an organic molecule, those that increase the energy mobilization and also those that reduce it, influence both the Arrhenius parameters: energy

activation (E) and pre-exponent (A) uniformly, *i.e.*, either increase or reduce both of them. In the framework of the effect considered in the present paper, both Arrhenius parameters are closely bound one to another quantitatively. Indeed, the mobilization of energy quantity ΔE from the internal energy of a molecule reduces simultaneously, for the same value (ΔE), both the energy activation (E) and the energy of the transition state. A decrease in the transition state energy for this value (ΔE) means also a decrease in its entropy for the value of $\Delta E/T$, pre-exponent (A) by a factor $e^{\Delta E/T}$ and logA for value $\Delta E/2.3$ RT. In the case of demobilization, all these values will be increased for the same quantities. In such a manner, the considered effect is bound to positive linear correlation between the logarithm of pre-exponent (A) and energy activation (E) with a correlation coefficient (b) equal to 1/2.3.RT. It is, of course, the approximate evaluation of this coefficient, based on the statistical regularities, which are not completely applicable for the dynamic picture that is being considered here. It can be shown that this is the top evaluation. At the real lower values of this coefficient (b), the low values of both the Arrhenius parameters correspond to the high values of the reaction rate (mobilization) and, conversely, the high values of both of them correspond to the low rates (demobilization).

It is interesting in this connection to consider the influence of different substituents in a molecule on both the Arrhenius parameters of the same reaction, that is, the correlation between both Arrhenius parameters of the one group of derivatives. The absolute majority of derivatives really shows a positive correlation between the energy activation (E) and the pre-exponent (A), which in the coordinates logA ~ E can be expressed as logA = a + bE. Such graphs are quite informative. The derivatives with structural elements, which promote internal energy mobilization, in many cases are actually located in the region of the low Arrhenius parameters at the left low end of the correlation line, where the reaction rate is higher, and those which promote demobilization are located in the right high end. Unfortunately, the significance of this information is limited by the influence of other effects, as much on the energy activation ($\pm$ I effect, conjugation) as on the pre-exponent (change in the transition state degree of freedom). In spite of these complications, the consideration of such graphs is useful, because the significant deviation from the correlation line is practically always very informative, as for instance, at the change of the reaction mechanism.

In spite of the generally qualitative character of the proposed method, as applied to derivatives it also allows some quantitative evaluations. This is particularly true of a qualitative evaluation of the energy quantity remaining

in the case of demobilization on the one degree of freedom for different types of structural elements (see below). These structural elements preserve a more or less similar value of internal energy surplus in the different chemical substantives, a fact that indicates the objective character of these evaluations.

The new concepts introduced by the proposed method are internal energy mobilization and demobilization and the regularity of the fluctuation energy passing in a molecule through different bond types; its reflection, dispersion and concentration on a certain type of bond seem somewhat unusual, although they represent the fundamental properties of the chemical kinetics. The appearance of a new relevant concept is always very important for any branch of the science. This paper is devoted to the elucidation of relevance of the new concepts.

The main items of the proposed concepts may be formulated briefly in the following way.

1) An organic molecule has structural elements that promote the internal energy mobilization for its unimolecular decay in the high-pressure region, reduce both Arrhenius parameters, and increase the reaction rate, and elements that, conversely, detain part of internal energy, disperse it, and impede its concentrations on the bond that is being broken. This second type of structural elements increases both the Arrhenius parameters and reduces reaction rate.

2) The mutual arrangement of these two types of structural element in the particular organic molecule produces the row regularities that are discussed in this paper.

3) A weak bond in the vicinity of stronger neighbouring bonds is an acceptor of their common vibrational energy in order to break. This bond represents the first type of structural elements that promote an internal energy mobilization.

4) The number of the linked identical bonds: the branching of the carbon chain or the bonds' ring represent the second type of structural element, which disperses internal energy between identical bonds and impede its concentration on the bond that is being broken. In the row: the primary, secondary, and tertiary carbon atom increases the number of linked identical bonds and increases also the energy dispersion.

5) The two types of the structural element, those that increase the energy mobilization and also those that reduce it, influence both the Arrhenius parameters uniformly, *i.e.*, either increase or reduce both of them simultaneously. This binds quantitatively energy activation (E) and A-factor (A) for the system of the derivatives. Each derivative either increases or reduces both of them. This correlation between both Arrhenius parameters for the derivatives system produces the row regu-

larities discussed in the present paper.

The discussion begins with examples of the mobilization of the internal energy of a molecule and continues with demobilization examples. Between the presentations of these two groups of examples, the kinetic data, which represent both tendencies, are presented. The inclusion of examples that are representative of both tendencies somewhat complicates the construction of the text.

2. DISCUSSION

2.1. The Thermal Decomposition of the Hydrazines and the Amines)

These are simple bond fission reactions. The comprehensive collection of kinetic data on the decomposition of the hydrazines and amines and their analysis is contained in the volume by Benson and O'Neal [7] mentioned above. First, they called attention to the fact that both Arrhenius parameters of these reactions are extremely low, being very far beyond the framework of the modern statistical theories. The authors do not find an explanation for this. They write: "The A-factors of the hydrazine and the amine decompositions are all less than the normal ekT/h values; some are significantly lower. Such a situation implies negative entropies of activation, which, in the case of simple bond fission reactions is just not reasonable." (page 34) The negative entropy of activation for bond fission reaction is typical of the increased energy mobilization in the high-pressure region, according to the effect being considered (see Introduction). High A-factors are presently more consistent with the modern theory of simple bond fission reactions, than are low A-factors. Such reactions as a rule have logA-factors higher than "normal" values (13.5 - 14), being about 15 - 16. At the same time the experimental values logA-factors of the hydrazines and the amines are as a rule lower than this "normal value, being 11.7 - 13.2 for hydrazines and a little bit higher for amines – 12.8 - 13.4, which means about 3 orders of magnitude lower than the majority of other reactions with a single bond rupture.

The simple bond fission does not demand a particular transition state conformation, reducing its degrees of freedom and accordingly reducing its entropy and A-factor. Therefore the low values of A-factor mean also a significant reduction in the rotational and vibrational energy remaining on the molecule and on the transition state, *i.e.*, in the significant internal energy mobilization for bond breaking in the high-pressure region.

Presently, the activation energy (E) of the bond fission reactions is universally accepted as the reaction enthalpy, *i.e.*, the kinetic factor is accepted as a thermodynamic one, which leads to many complications. This also means that the most common assumption has been that the activation energy for radical-radial recombination reactions is accepted as zero. This is more or less true with some precision for many bond fission reactions. At the same time, experimental values of the energy activation for the hydrazines decompositions are less than the reaction enthalpy by 10 - 14 kcal/mol and for the amines by 7.5 - 11. These values would probably represent the highest discrepancy of their kind known. This means that the activation energy of a molecule of a hydrazine or an amine is significantly lower than the strength of the bond that is being broken, *i.e.*, a part of the energy for bond breaking arrives from the internal energy of a molecule. This also confirms that the internal energy mobilization in the high-pressure region is in agreement with the considered effect.

Both the conditions for bond fission reaction that are accepted now, *i.e.*, the high value of the A-factor and the energy activation values exceeding bond strength in the high-pressure region, are the consequence of the statistical character of the modern kinetic theories. This character excludes any tendency for energy redistribution inside a molecule. This means that the transfer of an energized molecule to a transition state is governed by purely statistical consideration and its bond interaction, which is studied by dynamic methods, is practically ignored. Such indeed is the main concept of the modern statistical RRKM theory that defines the general approach of the collection's authors. Since the reported experimental data for hydrazines and the amines contradict significantly the statistical transition state theory, the collection's [7] authors presented also the preferred values of both the Arrhenius parameters (E and A-factor) adapted to this modern theory in such a way as to preserve the rate constant. They write: "Preferred values will generally be those judged to be most consistent with the experimental reaction rate and transition state theory" (page 5). The usual procedure has been to equate the activation energy to the reaction enthalpy and to increase also the A-factor to preserve the reaction rate. In this case, of course, the agreement between experimental and adapted reaction rates was preserved only at the mean reaction temperature, with a discrepancy for higher and lower temperatures.

The thermal decomposition of the hydrazines and amines, whose kinetic data are in the collection [7], were performed in the gas phase at the temperature 750 - 950˚K. The toluene carrier and aniline carrier techniques were employed. The thermal decomposition of hydrazine derivatives takes place by N-N bond breaking, in accordance with the scheme:
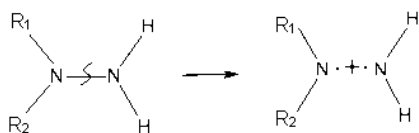
The rates were based on the production of ammonia. The reaction of 1,1-dimethylhydrazine. The experimental data: energy activation (E) is 49.6 kcal/mol; logarithm of pre-exponent $\log A = 13.2$; logarithm of constant rate k_T (sec^{-1}) $\log k_T = -0.88$ (770˚K). The heat of the formation of the produced radicals (heat of formation or broken bond strength) is calculated by the authors as $\Delta H˚ = 63.0$ kcal/mol. The authors notice: "Rate constants are probably reliable. Arrhenius parameters are low" (page 442). In such a manner, in this case, energy activation (E) is lower than bond breaking energy by 13.4 kcal/mol (a quarter of its value). The authors increased the preferred value of energy activation (E) up to about the heat of formation ($\Delta H˚$), i.e., up to 62.7 kcal/mol. They were forced to increase $\log A$-factor up to 16.9, i.e., by 3.7 units, in order to preserve the rate constant at the mean temperature (805˚K). This means the A-factor increases by five thousand times. For these preferred Arrhenius parameters, the value of the rate constant at 805˚K is preserved quite precisely.

Similar situations with other hydrazine derivatives. The experimental data of the methyl hydrazine decomposition are: energy activation is 51.9 kcal/mol; $\log A$ is 13.19 units; the calculated heat of formation $\Delta H˚$ is 65.6 kcal/mol. The authors increased the preferred value of energy activation up to about the heat of formation, 64.8, i.e., by 12.9 kcal/mol, and $\log A$ by 3.51 units up to 16.7 to preserve the reaction rate at the mean of temperature region.

Phenylhydrasine decomposition. The experimental data: $E = 40.0$ kcal/mol; $\log A = 11.8$. The calculated heat of formation $\Delta H˚ = 50.7$ kcal/mol is 10.7 kcal/mol more than experimental values of energy activations. The authors increased again the preferred energy activation up to about the heat of formation −51.1 kcal/mol and $\log A$ up to 15.5 unit, in order to preserve the reaction rate.

The main conclusion drawn from the kinetic data for hydrazine decomposition is that energy activations are significantly less than the strength of the bond that is being broken and A-factors are significantly less than "normal" values for bond fission reactions. The thermal decomposition of amines takes place with C-N bond breaking.
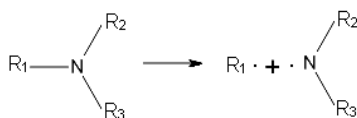
Here also, the experimental values of energies activation are lower than the breaking bond strengths and the A-factor is lower than "normal" values for the bond fission reaction, with a slightly smaller difference than for hydrazines. The experimental data for n-methylbenzilamine are: energy activation $E = 57.7$ kcal/mol; logarithm A-factor 12.86 units; calculated heat of formation $\Delta H˚ = 65.2$ kcal/mol. The authors increased the preferred value of the energy activation a bit more than heat of formation up to 69.0 kcal/mol, i.e., by 11.3 kcal/mol and $\log A$ up to 15.7 i.e., by 2.84 units, to save the reaction rate.

The experimental Arrhenius parameters of n-methylaniline: $E = 60$ kcal/mol and $\log A = 13.4$ units. The authors increased the preferred values to $E = 67.7$ and $\log A = 15.3$. The preferred E value is close to heat of formation $\Delta H˚ = 68.3$ kcal/mol. In both cases, the authors note that: "The rate constants are probably reliable. Arrhenius parameters are suspect".

The strength of the N-N bond in the hydrazine derivatives is about half of the surrounding C-C bonds. According to the considered effect, such a difference must lead to significant internal energy mobilization of a molecule for the weak bond that is being broken. In the case of hydrazines, the weak bond (N-N) is an energy acceptor and the strong bonds (C-N, C-C) are the energy donors. In the case of amines, the weak bond is C-N and the strong bonds are C-C. The internal energy mobilization must, in its turn, lead to a significant reduction in the energy that is necessary for molecular activation (E) and the entropy of activation.

The experimental data of the hydrazines and the amine decomposition give a few independent reasons for such a mobilization in the high-pressure region:

1) The energy activation of a molecule is lower than the strength of the bond that is being broken.

2) The A-factors for the hydrazines and amines decomposition are actually lower than A-factors for most bond fission reactions by about three orders of magnitude.

3) As mentioned in the Introduction, in the framework of the considered effect there must be a certain dependency between the lowering of the energy activation (ΔE) and that of the A-factor. The average energy activation of hydrazines decomposition is lower than the breaking bond strength by about 13 kcal/mol. According to coefficient $1/2.3 \cdot RT$, the lowering of $\log A$ by 3 - 3.5 units can be expected. The average experimental value of $\log A$ for hydrazines is about 12.5, which is actually less than "normal" values (15 - 16) for bond fission reactions by this value (3 - 3.5).

The situation for the amines is similar. Here the average experimental value of ΔE is about 9 kcal/mol, which

gives a correction for logA of 2 - 2.5 units. The experimental values of logA are 13 - 13.5, which is approximately less than the "normal" values (15 - 16) by this amount (2 - 2.5).

It is pertinent to note that the authors of the cited volume [7] adapted the experimental values of the logA-factors for the hydrazines and amines, practically up to these "normal" values for bond fission reactions (15 - 16).

4) So sharp an internal energy mobilization (~13 kcal/mol or about a quarter of the total activation energy) probably demands a remarkable energy activation for the back reaction of radicals' recombination, as is discussed in the Introduction. Benson and O'Neal in their volume [7] collect also recombination rate constants for nitrogen radicals. All nitrogen radicals whose recombination produces hydrazines and amines have values of logarithm rate constant (l/mol.sec) ranging from 5.8 to a maximum of 7.5 (lower values for hydrazines); the structurally similar hydrocarbon radicals have values ranging from 8.7 up to 9.8. Other nitrogen radicals also have these values ranging from 8.6 to 9.8. The recombination rate of radicals, which produce hydrazines by a 3.0 - 3.5 and amines by a 2.0 - 2.5 order of magnitude, is less than the absolute majority of other radicals, whose recombination energy activation are now accepted as being zero. This means that the radicals that produce the hydrazines and amines have a remarkable obstacle to their recombination in the form of significant energy activation. These data are not fully independent evidence of internal energy mobilization because some of them are calculated from the results of the hydrazines and amines' decomposition.

5) The recombination rates data of the radicals that produce the hydrazines and amines make it possible to estimate the energy activation (E) of these reactions. The factor $e^{-E/RT}$ reduces the values of recombination rate by a 3 - 3.5 order of magnitude for hydrazines and by 2 - 2.5 for amines. The energy activations (E) of the radical recombination from this equation are very close to the internal energy mobilizations of the decomposition, *i.e.*, about 13 kcal/mol for hydrazines and about 9 - 10 for amines. Such a relationship between the kinetics of the direct and back reactions must be available in the framework of the considered effect. This means that direct and back reactions are accelerated similarly (a purely kinetic effect).

The true cause of the remarkable energy activation for nitrogen radicals' recombination lies far beyond the scope of the present article. Only one of a few possibilities can be mentioned. A hydrazine molecule is constituted of two dipoles. Their positively charged ends (nitrogen atoms) are bound one to the other by the N-N bond. The repulsion of these dipoles after N-N bond breaking forms a back slope on the potential energy curve of the N-N bond. It is also the reason for the activation energy arising in the back recombination reaction. The dipole is formed by a positively charged nitrogen atom that is found in the vertex of a trigonal pyramidal structure and a negatively charged single non-bonding pair of electrons in its base (sp^3 hybridization). The two orbitals of the nitrogen covalent bonds and one orbital of nitrogen's lone electron pair form the three arms of this trigonal pyramidal structure.

The existence of a few independent pieces of evidence of internal energy mobilization for the bond that is being broken in the high-pressure region for the hydrazine and amine makes this mobilization mechanism quite reasonable. It contradicts statistical theories and reflects the general dynamic picture of the bonds interaction according to the proposed concept.

To the best of our knowledge, the very serious discrepancy mentioned above between theory and experiment for hydrazine and amine [7] has not been satisfactorily explained until now.

It is quite possible that the consideration of the discussed effect applied to other substances and reactions will bring about a revision of the same assumptions, which are accepted now *a priori*:

1) The high values of both Arrhenius parameters for bond fission reactions;

2) The equality of the reaction enthalpy and the energy activation for the bond fission reaction and the consequent absence of activation energy for the back reaction of radicals recombination;

3) Other conclusions in the kinetics and thermodynamics, that are bound to the above mentioned assumption.

2.2. Decomposition of Nitroalkanes

The thermal decompositions of the nitroalkane proceed through a five-center transition state, producing olefines and nitrous acid:
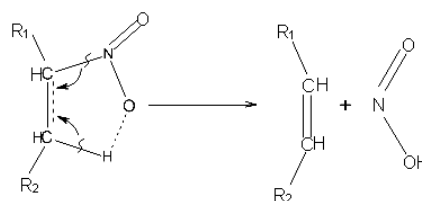
The temperature region for this investigation is, as a rule, 600 - 700˚K. The reaction rates are surface-sensitive, and therefore the reaction chamber walls were conditioned and, if necessary, radical chain reactions were inhibited, to be sure that the residual reaction is molecular. The reduction in activation entropy in these reactions

is a natural result of the restriction in the internal rotation of a transition state. At the same time, this reduction was significantly greater than can be theoretically estimated on the basis of the statistical transition state theory, (RRKM). Benson and O'Neal write in their collection [7]: "By the transition state methods used to estimate A-factor for the four- and six-center reactions, the A-factor estimates of the five-center reactions are between one and two orders of magnitude higher than those reported" (page 12).

The reported value of logarithm A-factors for the thermal decompositions of nitroethane are 11.35; 11.53; 10. 83; 13.0; 12.4. Benson and O'Neal write: "The experimental A-factors require an extremely tight activated complex (*i.e.*, almost total loss of both internal rotations). By analogy with six-center transitions state reactions, one would expect an A-factor in excess of 10^{13} sec^{-1}" (page 130), *i.e.*, logA is more than 13. The experimental A-factors for 2-nitropropane decomposition are 11.34; 11.05; 11.05; 11.30. Benson and O'Neal write: "Arrhenius parameters appear unreasonably low" (page 132).

In the reaction of nitroalkane decomposition, the weak C-N bond (73 kcal/mol) is broken in the surrounding of stronger bonds: the double N=O bonds (about 140 kcal/mol) from one side and one or two C-C bonds (83 kcal/mol each) from the other. The non significantly stronger C-C bond, however, in the process of this reaction is significantly reinforced at the sacrifice of the weakening C-N (scheme above) and is converted into a double C=C bond (145 kcal/mol), in just the most critical position, defining the internal energy mobilization of a molecule. So that, in this position, when the configuration of a nitroalkane molecule approaches the transition state conformation, the weakened C-N bond that is being broken is surrounded by very strong bonds.

In addition, the limitation about the obligatory presence of the energy activation for a back reaction as for a simple bond fission is absent here. The energy redistribution here takes place inside a transition state ring, and the forming molecules, as distinct from radicals, always have remarkable energy activation for a back reaction. This leads one to expect significant internal energy mobilization and consequently a reduction in the A-factor, as has been shown experimentally for nitroalkanes.

This is an example of the weak bond breaking in the neighborhood of stronger ones in the ringed transition state, which leads to additional internal energy mobilization and A-factor reduction.

2.3. The Thermal Decomposition of Tetra-Alkyl Orthosilicates (Silicon Alkoides)

The tetraalkyl orthosilicates $Si(OR)_4$ and other ele-

ments of the IV group (C, Ge, Sn, Pb) are also important for kinetic investigation, because they make it possible to vary widely both the nature of the central atom and also the radical (R) structure.

The replacement in the $Si(OR)_4$ of methyl radical (R) instead of ethyl leads to very significant kinetic consequences. For this reason Chu, Breslin, Wang, Lin, and co. investigated [10,11] the relative stabilities of tetramethyl (TMOS) and tetraethyl orthosilicate (TEOS). The pyrolosis was carried out between 858 and 968 K for TMOS and between 721 and 820 K for TEOS, with a very low concentration of the reagents, using argon as diluent and near atmospheric pressure to minimize the reactor wall effect and to obtain a reliable first order rate constant in the high-pressure region.

The rate constants for TMOS can be effectively represented by k = $1.4.10^{16}$ exp(−81200/RT) sec^{-1}, consequently logA = 16.15 and E = 81.2 kcal/mol. The rate constant for TEOS is k = $7.4.10^{10}$ exp(−49500/RT) sec^{-1} steps in these two systems are very different. The A-factor of the TMOS reflects a very loose transition state, typical for a bond-breaking process producing radical products: $Si(OCH_3)_4 \rightarrow \cdot CH_3 + \cdot OSi(OCH_3)_3$. The low A-factor and activation energy measured for TEOS suggest that the initial decomposition may occur by a six-centered complex:
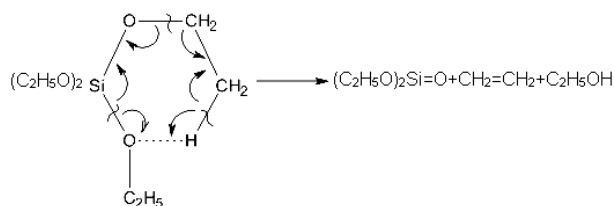
The possibility of such a mechanism is connected to the presence of β-hydrogen in the TEOS molecule. This mechanism is similar to the known 6-centered molecular decomposition process for diethyl carbonate:
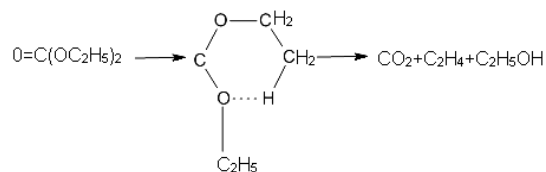
whose unimolecular decomposition constant has been measured to be K = 7×10^{13} exp(−4600/RT) sec^{-1}. The authors are confused that they obtained an A-factor of the TEOS significantly lower (three orders of magnitude) than the A-factor of diethyl carbonate and other six-centered reactions. They refer also to the opinion of Benson and O'Neal that the typical A-factors for the 6-centered molecular elimination process are 10^{13} - 10^{14}

s^{-1} but not 7×10^{10}. They suspect the secondary reaction's influence is an explanation for this discrepancy. Benson and O'Neal write in section 4.1, which is devoted to six-centered elimination reactions: "Observed entropies activation are about half this expected amount; therefore cyclic transition states must be reasonably loose" (pages 12-13).

The strength of the C-O bond that is being broken is 80 - 85 kcal/mol. The strength of the neighbouring Si-O bond is not less than 100 kcal/mol [10] and it is significantly reinforced in the process of this reaction, transferring into double bond Si=O. Therefore, the weak C-O bond being broken is neighbouring on a very strong bond, exactly at the critical moment when the former is found in its anharmonic region. In such a manner, the mobilization of the internal energy of a molecule in the high-pressure region may quite easily be the cause of the unusually low values of the A-factors for these reactions.

Both the Arrhenius parameters of the TEOS pyrolysis are significantly lower than the TMOS one, and the constant rate is significantly higher. The transition to a kinetically more advantageous mechanism leads to a reduction in both the Arrhenius parameters in the same fashion as the influence of the considered effect. However, this transition is accompanied by a much more significant reduction in energy activation in relation to the reduction in the A-factor. This leads naturally to a very remarkable rate constant increase. Therefore, this transition in the coordinates logA~E for some derivative systems will be characterized by a deviation from the correlation line to the side of the higher A-factor at the same energy activation, *i.e.*, up and leftward. Such a deviation is a clear indication of the transition to another reaction mechanism.

Actually, in the transition from the TMOS pyrolysis to the TEOS one, the energy activation is reduced by 31.7 kcal/mol. The correlation coefficient between E and logA (1/2.3·RT) equals $\approx$ 0.24 mol/kcal for an average experimental temperature of 900 K. The reduction in the logA may be expected, in the framework of the considered effect, to be by a value of $31.7 \times 0.24 = 7.7$ units, *i.e.*, from 16.15 down to 8.45 units. The real value of the logA-factor is actually remarkably higher −10.87 units. For derivatives decomposing as a TMOS according to the simple bond fission mechanism, the represented TEOS point must be significantly deflected from the correlation line to the upper left side, which will be the indication of reaction mechanism change.

This is also an example of the weak bond breaking in the ring in the vicinity of the stronger one, which leads to a significant reduction in the Arrhenius parameters.

It is also an example of the change in the reaction mechanism drawing the derivate out of the correlation line.

2.4. The Influence of the Continuous Chain Length on the Internal Energy Mobilization

It is of interest to consider the substances whose molecules contain both structural elements, which, just as they promote internal energy mobilization, also suppress it. Among these are, in particular, alkanes containing the t-butyl group, which is bound with a continuous chain. The strongly branched t-butyl group
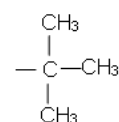
detains energy fluctuations on its bonds (demobilization) while the continuous chain promotes the internal energy concentration on its bonds (mobilization).

The availability of the back slope on the potential energy curve in this case of the two contrary influences is probably less critical than for other cases of mobilization.

The influence of the length of the continuous chain radicals (R) on the main kinetic parameters of the bond breaking between this radicals and the t-butyl in the molecules with a common formula, R-t.butyl, is studied by W. Tsang and J. Kiefer [12] and [13]. The main parameters of this reaction for different alkanes with this common formula were studied under strongly comparative conditions. This increases the precision of the comparison and may reveal a tendency that is of interest to us, even though the difference between the results is not big.

The comparative data for these alkanes' decomposition were determined from a single pulse shock tube study at a temperature of 1000 - 1200°K. This very low-pressure pyrolysis (VLPP) method is a very good one for obtaining reliable first-order parameters in the high-pressure region for simple bond fission reactions. The bond fission, an initial reaction in decomposition, is, as a rule, complicated by the numerous secondary reactions of the radicals that are produced. The good solution is a very short reaction time and accordingly a very low rate of conversion and concentration of the radical that is produced. The single pulse shock tube was designed and constructed to achieve extremely short reaction times and conversions.

The logarithm of A-factors for methyl, ethyl and n-hexyl groups (R) were: 17.0; 16.778; 16.477. These values have a tendency to reduce with the increase in the continuous chain's length. The situation of energy activation is similar: 81.4; 76.8; 74.1 kcal/mol. In spite of

the moderate difference between A-factors, the common tendency is clear. The continuous chain lengthening increases the internal energy mobilization.

The chain increase for one carbon atom from methyl to ethyl radicals reduces the logA by 0.22 units. The subsequent chain length increase reduces more moderately. This influence fades along the chain's length.

In this case, the chain's increase for one carbon atom close to the breaking bond is equivalent to an internal energy mobilization equal to 2.3·ΔlogA·RT = 2.3·0.22 RT ≈ 0.5 RT. This is, of course, a very rough estimation.

This is an example of the carbon continuous chain lengthening promoting the internal energy mobilization.

2.5. The Thermal Decomposition of the Cyclobutane and Its Derivatives

This is a homogeneous unimolecular reaction yielding two molecules of olefins. The reaction is expressed by the following scheme:
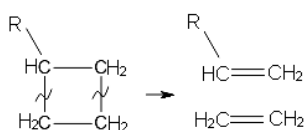
Presently, the biradical mechanisms are commonly accepted, in particular because simultaneous breaking of two opposite ring bonds does not agree with the high A-factor. The logarithm of A-factors as a function of energy activation (E) for cyclobutane derivatives with this common formula $R-C_4H_7$ is shown in **Figure 1**. The reaction is studied in the temperature region 695 - 740°K. The connection between these two parameters is very well expressed by the correlation line:

$$logA = 2.12 + 0.216·E,$$

with a moderate deviation from it. The correlation coefficient equal to 0.305 corresponds to the preservation of the constant reaction rate along the whole correlation line. The real, lower correlation coefficient, 0.216, corresponds to the reaction rate increase in the left lower part of the correlation line, where the simultaneous decrease of both the Arrhenius parameters reflects the mobilization of the internal molecule energy for bond breaking. Indeed, at a temperature of 720K the rate constant for methylcyclobutate (point 1) in the lowest part of the correlation line is $5.5 × 10^{-4}$ sec^{-1}. At the same time, t-butylcyclobutate (6) in the highest part of the correlation line has a lower rate value: $2.58 × 10^{-4}$ sec^{-1}.

All the derivatives that appear in **Figure 1** can be divided into two groups, those lying below and those lying above cyclobutane (4), *i.e.*, more to the left and more to
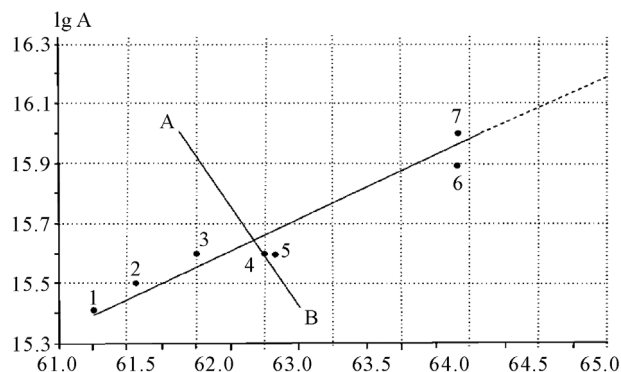

Figure 1. The logarithm of A-factor as a function of energy activation (E) for cyclobutane derivates: 1-methylcyclobutane; 2-propylcyclobutane; 3-ethyl cyclobutate; 4-cyclobutate; 5-isopropylcyclobutane; 6-t-butylcyclobutate; 7-cyclobutane d8.

the right of the line AB. The derivatives with continuous-chain substitutes methyl, ethyl and proplycyclobutanes lie to the left of and below cyclobutate (4), in the region corresponding to the internal energy mobilization of a molecule for the ring bonds breaking. Both the Arrhenius parameters in this region are lower and the reaction rate is higher than for derivatives on the right side of the correlation line. A substitute branching shifts a derivative right and upward along the correlation line. The most branched t-butylcyclobutate is found in the almost highest position (6); the less branched isopropylcyclobutane is found lower (5).

Cyclobutane has a high rate of symmetry and completely identical C-C bonds, which, according to the effect being considered, promotes the dispersion of energy fluctuation into the ring and hampers the energy concentration on its bond. The cyclobutane ring is a factor of the demobilization. Any substitute reduces its symmetry rate and must therefore reduce the A-factor. In spite of this, t-butyl significantly increases them (6), that reflects the very high-energy dispersion ability of the strongly branched chain. These two opposing influences on the less branched isopropylcyclobutane (5) only reciprocally counterbalance one another, so that it is found practically on the same part of the correlation line as cyclobutane (4).

Some conclusions about the dynamical influence of the C-H bonds on the C-C ones can probably be drawn from these data. This influence, from the viewpoint of mobilization as well as that of demobilization, has to be less than the mutual influence of C-C bonds, because their parameters, and primarily all masses and frequencies, are significantly different. The substitution in a hydrocarbon of a hydrogen atom for deuterium approaches a little these parameters. In this connection, a deuterated compound has to increase its dynamic influ-

ence (mobilization or demobilization) in comparison with an initial hydrocarbon. The deuterated cyclobutate (7) has a remarkably higher rate of demobilization, and it is found significantly higher on the correlation line.

The broadening of a derivative group included in the correlation picture increases, as a rule, the results' deviation from the correlation line. The inclusion of the derivatives with two substitutes, for example 1.2 dymethylcyclobutanes, in the above correlation as well increases the deviation from the correlation line, to a large extent for trans-compound and to a lesser extent for cis.

The 1,1,3,3-tetramethylcyclobutane, with its high rates of symmetry and a branching, is found practically on the continuation of the correlation line in the demobilization region (dotted line). This cyclobutane derivative, according to the effect being considered, actually must show a high rate of demobilization.

The influence of the continuous-chain substitutes (1,2,3) in this case, except of a mobilization, is probably above all expressed in the reduction in the demobilization influence of the cyclobutate (4). So that the derivative for which both the influences mobilization and demobilization are counterbalanced lies near to these three derivatives (1,2,3) or even lower on the correlation line. This frontier derivative can have both its Arrhenius parameters maximum close to their estimation based on statistical theories (for example, RRKM), without the dynamical influence.

Generally, the analysis of such a correlation picture for a derivatives system may give some kinetic information that is useful, and even more specific for a narrower group of derivatives.

There are here the derivatives that, according to the proposed concept, promote the internal energy mobilization and those that impede it. The first group lies in the lower part of the correlation line (with low E and A values) and the second one in the higher part.

2.6. The Pyrolyses of Esters to Give Olefins plus Carboxylic Acids

The esters decompose as a rule by purely molecular mechanisms with some exceptions for primary esters, which demand that a concurrent chain reaction be suppressed by inhibitors for this. For the unimolecular process, the six-centered transition state is commonly accepted:
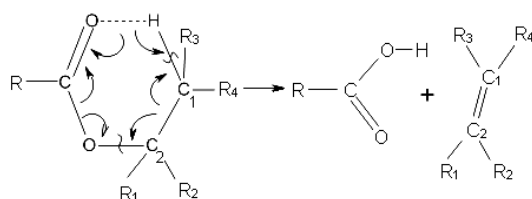
Inside the transition state ring, a very significant vibrational energy redistribution takes place. The strengthening bonds C-O and C_1-C_2 and the forming O-H bond transfer their released energy to the C_1-H and C_2-O bonds that are being broken (the energy flow is indicated in the scheme by arrows). In the acid part of the ring, the simple C-O and the double C=O bonds exchange places. This is related to the energy exchange between them. This affects the other bonds of the transition state ring to only a moderate extent. The breaking of the bonds (C_1-H and C_2-O) takes place in the alcohol part of the ring. For this reason alone it is possible to assume that the molecular structure of the alcohol part of an ester influences the ester's decomposition more significantly than the structure of the acid part (see below).

All the energy released at the conversion of the simple C_1-C_2 bond into the double C_1=C_2 bond (~60 kcal/mol) and the O-H bond formation (~100 kcal/mol) passes through the carbon atoms C_1 and C_2 on the bonds that are being broken, C_1-H and C_2-O. In the framework of the effect considered here, the branching at these carbon atoms C_1 and C_2 must have a significant influence on this passage, hampering it. For example, the split of the sole energy flow through the C_1 carbon atoms in the direction of the side chains, R_3 and R_4 (see scheme) reduces the energy entering on the bonds that are being broken in the ring, C_1-H. A similar situation exists with regard to the C_2 carbon atom and the branching into the R_1 and R_2 side chains. In other words, the reduction in the alkyl substituent's numbers around the double C_1=C_2 bond in the reaction product accelerates the production of this product from the viewpoint of the effect being considered here. In such a manner, the effect explains the well-known Hofmann rule of which this is a special case. Robinson and Holbrook [8] formulate this rule: "For esters which are capable of decomposing in different ways, the predominant direction of elimination is given by the Hofmann rule, *i.e.*, the favored olefinic product is that bearing the fewest alkyl substituents around the double bond." The influence of the usual steric effect is also possible in this case.

The correlation picture of the esters' decomposition in the coordinates $\log A \sim E$ is split into three almost parallel separate lines depending on the molecular structure of the alcohol part of the molecule where the bond breaking is taking place. The deviation from the correlation lines is moderate, whereas the difference between them is very significant, and it shows the very significant influence of the structure of the alcohol part of a molecule, **Figure 2**. In so doing, the derivate's position is practically almost independent of the structure of the acid part of its molecule. The lowest correlation line (AB) corresponds to the continuous chain alcohols and has minimum
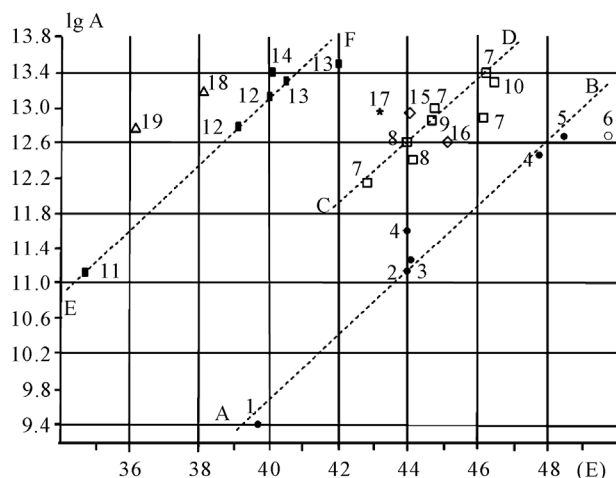
Figure 2. The correlation between high-pressure Arrhenius parameters for the pyrolyses of the esters, to give olefins and carboxylic acids. Designation: - • - continuous-chain alcohols; - □ - isopropyl alcohols ; - ■ - branched-chain alcohols (at the tertiary carbon atom); - ◇ - cycloalkane alcohols; -✶- aromatic alcohols; - △ - t-butyl chloroacetates. 1-propyl formate (9.4; 39.7). 2. ethyltrimethylacetate (11.2; 44.0). 3. ethyl formate (11.3; 44.1). 4. ethyl acetate (11.6; 44.0). 4. ethyl acetate (12.5; 47.8). 5. ethyl propionate (12.7; 48.5). 6. ethyl-d$_5$ acetate (12.7; 49.5). 7. isopropul acetate (12.1; 42.9). 8. isopropyl formate (12.4; 44.2). 8. isopropyl formate (12.6; 44.0). 9. isopropyl trimethylacetate (12.9; 44.8). 7. isopropyl acetate (12.9; 46.1). 7. isopropyl acetate (13.0; 45.0). 10. sec-butylacetate (13.3; 46.6). 7. isopropylacetate (13.4; 46.3). 11. t-butyl formate (11.1; 34.6). 12. t-butyl propionate (12.8; 39.2). 12. t-butyl acetate (13.3; 40.5). 14. t-amyl acetate (13.4; 40.3). 13. t-butyl acetate (13.5; 42.1). 15. cyclopentyl acetate (12.9; 44.1). 16. cyclopentyl acetate (12.6; 45.2). 17. 1.2 diphenylethyl acetate (13.0; 42.3). 18. t-butyl chloroacetate (13.1; 38.1). 19. t-butyl dichloroacetate (12.8; 36.1). The first figure in the brackets is logA, the second one is E kcal/mol.

A-factors from all three groups. The alcohols with minimum branching of the carbon chain (at the secondary carbon atom) are found on a somewhat higher level of A-factors, line CD.

The maximally branched alcohols (tertiary carbon atom) are found in the highest position along the logA axis, with average logA values for 3.2 units higher than the continuous-chain alcohols - line EF (**Figure 2**).

So clear a split of the common correlation line into a few separated, clearly distinguished groups, depending on some parameters, appears quite seldom and testifies to the distinct influence of these parameters. These data are in the very good agreement with the effect being considered here. As indicated in the Introduction, the branching disperses the energy fluctuation into different ways and hampers its concentration on the bond that is being broken. This increases the energy remaining on a molecule at the moment of breaking, *i.e.*, increases the A-factor and the energy, which is necessary for the mo-

lecule's energization (E).

It is possible, very roughly, to estimate the energy amount remaining on the branched groups, based on these data. The tertiary branching increases logA for 3.2 units, *i.e.*, 3.2 × 2.3·RT = 7.36·RT kcal/mol energy, which remains on this branched group. If we assume the main model of tertiary branching the t-butyl group (four carbon atoms, 12 degrees of freedom), then each degree of freedom of such very strong branching detains 7.36/12 = ~0.6·RT additional energy. No account has been taken in this calculation of the contribution of the C-H bonds, which have very different parameters (frequencies and strengths) from the C-C and C-O bonds. The average energy amount remaining on the secondary carbon atom branching can also be evaluated in a similar way. The propyl group may be taken as a main model of this branching (3 carbon atoms, 9 degrees of freedom). This branching increases the average logA value for ≈ 1 units (**Figure 2**), *i.e.*, the remaining energy for 2.3·RT or ~0.25 RT for each degree of freedom. This is significantly less than the stronger tertiary branching.

It is quite clear that the hydrogen atom and C-H bonds contribute somewhat to additional energy retention on a molecule at the moment of breaking. For this reason, the deutering, which to some extent brings together C-H and C-C bonds' properties, according to the considered effect, has to make some contribution to the A-factor's increase. The deutered ethyl-d$_5$ acetate (6) really has some more A-factor than the initial one (4) and lies therefore on the highest part of the correlation line (AB) for continuous chain alcohols. A similar situation pertains to deutered cyclobutane (see above).

A few additional esters are presented in the graph for comparison with their three main types (esters of primary, secondary and tertiary alcohols). The esters of cyclo alkanes, cyclopentyl and cyclohexyl acetates (15,16) are found practically on the correlation line CD of the secondary alcohol esters. The ester of the aromatic alcohol-1,2-diphenyl ethylacetate (17) - is found a bit nearer to the more branched tertiary alcohol esters. This can serve as a hint that the rings of cycloalkanes and aromatic compounds, containing bonds that are similar or almost similar to branched alkanes, refer also to some type of fluctuation trap and detain on these bonds part of the energy necessary for bond breaking. This of course merits more detailed consideration here (see below).

Contrary to the branching in the alcohol part of an ester, such branching has practically no influence when it is found in the acid part. Ethyl trimethyl acetate (2) with maximum branching in the acid part and ethyl formate (3) with the simplest acid part have practically the same A-factor values (their logarithms are 11.2 and 11.3) and lie on the same correlation line AB, practically on the

same point. A similar situation exists for isopropyl formate (8) and isopropyl trimethylacetate (9), where alcohol residua are the same (isopropyl), but acid ones are very different by the branching rate. They also have close A-factor values and lie on the same correlation line CD.

Even the very significant change of the acid residuum is connected to only a moderate deviation from the correlation line, corresponding to the same alcohol part of esters. The Arrhenius parameters of t-butyl chloroacetates (18, 19) lie not far from correlation line EF of the t-butyl esters that are not chlorinated. These deviations from the EF line are significantly less than the difference between the lines depending on the structure of the alcohol parts (AB, CD and EF).

In such a manner, the presence of the carboxyl group between two alkane chains hampers the fluctuation energy passing from the one carbon chain to the other, *i.e.*, from the fluctuation trap (isopropyl, t-butyl groups) in the acid part to the bond that is being broken in the alcohol part of a molecule. This reduces the efficiency of the fluctuation trap, *i.e.*, its ability to increase both Arrhenius parameters. It is indicated in the Introduction that the presence between two carbon chains of the bonds and atoms whose properties (frequencies, strengths, atomic masses) are significantly different from carbon-carbon bonds must lead to such results.

The proportionality coefficient "b" between logA and E, *i.e.*, the slope of the correlation lines AB, CD and EF in **Figure 2** equal ≈ 0.37. This generally corresponds to the temperature diapason for esters pyrolyses (500 - 800°K) according to estimation b = 1/2.3 RT.

The reported data dispersion of energy activation (E) and A-factor (A) by different authors is, as a rule, much bigger than their rate constant data. Therefore, between the results of different authors for A and E values of the same reaction, there exists, as a rule, a more or less linear correlation, approximately preserving a similar rate constant value. This correlation is quite near to those that are stipulated by the effect being considered. For example, all the four points of indicated data of the different authors for pyrolyses isopropyl acetate (7) are near to the correlation line CD for other derivatives with the isopropyl group (**Figure 2**).

The experimental data presented on Graph 2 are quite consistent with the body of conclusions about the effect being considered mentioned in the Introduction:

1) The influence of the carbon chain branching on the increase of both Arrhenius parameters for unimolecular reaction in the high-pressure region;

2) The increase in this influence with the increase in the branching rate;

3) The known Hofmann rule finds its substantiation in

the considered effect;

4) The influence of a heteroatom in a carbon chain between a branching and a bond that is being broken;

5) The linear character of the correlation line for a derivatives system in the coordinates logA ~ E.

2.7. The Benzene Ring as a Fluctuation Trap

The dynamics of intramolecular energy flow in the benzene ring is being studied very widely by the method of collision-induced relaxation of vibrationally excited molecules (at least many tens of articles). Therefore, there are enough data to look at this problem from the viewpoint that is interesting to us. The toluene molecule is a particularly attractive one to study because of the presence of both a benzene ring and a side chain. Most authors study the collision-induced dynamics of highly vibrationally excited toluene interacting with argon, using quasiclassical trajectory calculation [1,5] with the reproduced model **Figure 1**. Either CH_{methyl} or CH_{ring} has been set at its high-energy state (as a rule, a little bit below its dissociation threshold), while all other vibrational modes are in their ground state.

It is found [5] that the interaction near $\theta = 77°$ (**Figure 3(b)**) plays a dominant role in promoting energy loss through intramolecular energy redistribution, because it is connected with energy transfer by bend mode through the most flexible $C-C-H_{methyl}$ region. The smaller and greater angles lead to significantly less energy loss, because the attack of the incident atom in these cases is directed to the much more rigid corners of the benzene ring and not to the side chain. The reverse situation, *i.e.*, the excitation of the bend mode of the side chain region from the vibrational energy of the rigid benzene ring, seems significantly less probable. This is consistent with the well-known experimental fact that the highly excited benzene derivatives, which have side chains, show a much greater tendency to transfer their vibrational energy to translation than the highly excited benzene does (up to ten times as much).

The main conclusion to be drawn from these studies [1,5] is that the relaxation process is dominated by the energy flow from the side chain (methyl group) to the benzene ring, but not in the opposite direction. The authors [5] write: "We do not find any evidence of energy flowing out of $C-H_{ring}$ and returning to $C-H_{methyl}$. That is, energy flows irreversibly out of the initially excited $C-H_{methyl}$ vibration and deposits in the $C-H_{ring}$ after passing through two stretching and three bending modes" (page 4864). These two notions: "irreversibility" and "vibrational energy deposit" are exactly the key concepts of the considered effect.

The benzene ring has many properties to make it a practically perfect fluctuation trap: the almost identical

(a)

(b)
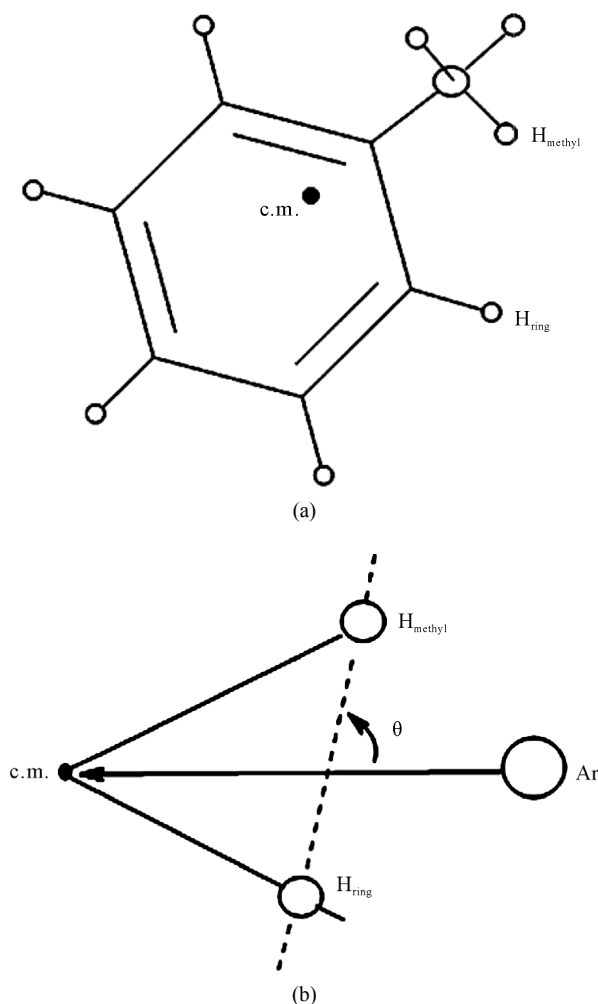
bonds, and the angles between them and their surrounding; the flat hexedron right form; and the identical mass distribution (six identical carbon atoms). All these properties are conditions for practically free fluctuation energy movement inside the ring, whereas their exit from the ring is very hampered, because of the demands of the side-chain bend mode excitation. At the same time, a side chain of aromatic compounds has the bond (β), which is very much weakened in comparison with the neighbouring one (α) as result of the I-effects of the benzene ring (about 63 against 90 kcal/mol).
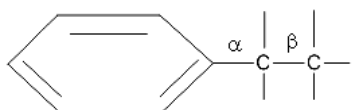
This bond (β) is broken in most bond fission reactions. The nearness of a weak bond, which mobilizes surrounding energy, must reduce the role of the benzene ring as a contrary factor.

These investigations [1,5] also give valuable informa-

tion about the C-H bond influence on the processes of concentration and dispersion of vibrational energy in the system of C-C bonds. The highly excited C-H$_{methyl}$ bond of toluene makes at least 15 vibrations before the collision with the Ar atom and ~30 after it, without any visual indications of this high energy transfer to neighbouring C-C bonds, which have significantly less vibrational energy, because they vibrate in their ground state [1, **Figure 2(a)**, page 1225]. This is so even in spite of the fact that the excited C-H bond in this case is in its anharmonic region and therefore vibrates at a lower frequency (484 cm^{-1}) than the neighbouring C-C bonds (1208 and 1494 cm^{-1}), which are in their ground state. A similar situation is described in [5]. 5, page 4863, **Figure 5**. The main role here is played, of course, by the mass difference between carbon and hydrogen atom. It should be noted that the highly excited C-C bond transfers its energy to surrounding C-C bonds practically during a few vibrations.

The vibrational energy from the excited stretch mode of the C-H$_{methyl}$ bond transfers to the C-H$_{ring}$ through two stretch modes of C-C bonds and deposits on this C-H$_{ring}$ bond to a greater extent than on these two intermediate C-C bonds [1, **Figure 2(b)**, **(c)**, page 1225].

These data, which are interesting for our consideration, have been taken directly from the corresponding graphs because the authors of these papers [1-5] discuss in the text other aspects of these calculations in which they were interested. All these data mean that the interaction between C-H and C-C bonds is significantly lower than between C-C themselves and C-H themselves. It can be loosely said that the vibrational energy movement inside a molecule takes place through the system of C-H bonds and the system of C-C bonds to some extent independently. This statement is significantly more right for the system of C-C bonds. The energy movement along C-H bonds fades much more quickly, because it must pass through C-C bonds with very different properties.

The main conclusion is that the identical bonds of the benzene ring constitute a very effective fluctuation trap, which disperses energy fluctuation and impedes its concentration on the individual bond of the ring or the side chain.

The second conclusion is that the interaction between C-C and C-H bonds systems is much weaker than the interaction inside the system of the C-C bonds and between the C-C bonds themselves.

It is of interest to compare the kinetic parameters of α and β bonds fission. The fission of an α-bond that neighbors the benzene ring must, to a significantly greater extent, reflect the true influence of the ring as a fluctuation trap, *i.e.*, its ability to increase A-factor and energy activation. The β-bond fission is a subject to two

contrary influences: the mobilization of the internal energy of a molecule by this weak *β*-bond for its breaking, and, in contrast, the detention of a part of this energy by the benzene ring. Unfortunately, the *α*-bond fission in the hydrocarbon benzene derivatives with the availability of the *β*-bond is almost impossible. In this case, the weak *β*-bond is practically always broken. There are, however, quite reliable data for an *α*-bond fission in the benzene derivatives containing a heteroatom. It is also of interest because the benzene ring properties as a fluctuation trap have to be quite manifest in this case also.
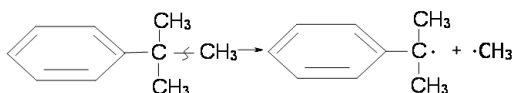
2.8. The *β*-Bond Fission

The *β*-bond fission can be considered in the example of the thermal unimolecular decomposition of ethylbenzene, isopropylbenzene, and tert-butylbenzene [14]:
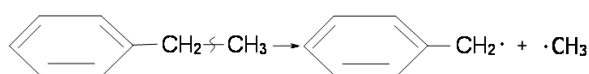
logA = 15.3; E = 72.7 kcal/mol; T = 1053 - 1234˚K
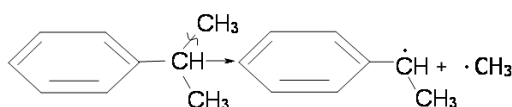
logA = 15.8; E = 71.3 kcal/mol; T = 971 - 1151˚K

logA = 15.9; E = 69.1 kal/mol; T = 929 - 1157˚K

These reactions have been studied using the very low-pressure pyrolysis (VLPP) technique under comparative conditions. Each reactant is decomposed by *β*-bond homolysis, producing methyl radicals and benzyl or benzylic type radicals.

The tendency of the A-factor to increase in passing from the ethyl to the t-butyl group is undoubtedly connected with the growth of the branching rate in this row. This regularity was already mentioned in particular for the esters pyrolyses and will be discussed further. Here the transfer from strongly branched t-butyl to the continuous chain of the ethyl group reduces the logarithm of A-factor to 0.6 units only, whereas a similar transfer for esters pyrolyses lowers this value to 3.2 units. This might quite easily be a consequence of the fluctuation trap influence produced by the benzene ring, which does not allow the reduction of A-factor. That is, the influences of the strongly branched t-butyl group and the benzene ring are quite commensurable and opposed.

The conclusion: The growth of the demobilization factor (dispersion rate of the fluctuation) occurs together with the increased number of identical bonds in the branching (branching rate).

2.9. The α-Bond Fission

The α-bond fission can be considered in the example of the unimolecular decomposition of nitrosobenzene with phyenyl radical production [15].
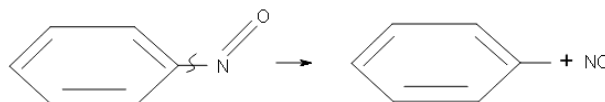
The rate constant was measured at temperatures between 553 and 648˚K at atmospheric pressure and a strong dilution with argon. This leads to minor secondary processes and a reliable measurement of the high-pressure first-order rate constant for the primary nitrosobenzene decay. The result of the experiments may be presented as energy activation 55.06 ± 1.08 kcal/mol, which is higher by as much as 6 kcal/mol than those reported earlier, and a logarithm A-factor of 17.15 units. Such a high A-factor value indicates essential vibrational energy dispersion inside the molecule, *i.e.*, the presence of an effective fluctuation trap, a role which, in this case, may be played only by the benzene ring.

The C-N bond that is being broken lies in the same plain as the benzene ring, and forms identical angles (~120˚) with both ring bonds. All this must promote the energy exchange between the C-N bond and the benzene ring and increase the efficiency of the benzene ring as a fluctuation trap in relation to this bond. The absolutely symmetrical phenyl radical is produced in the process of the nitrosobenzene decay, which may be a main factor in the vibrational energy dispersion inside its identical bonds (see below). This may probably justify the high A-factor value, in spite of the weak bond breaking, and confirm the high level of efficiency of the benzene ring as a fluctuation trap. This is consistent with the previous example. At the same time, all these preliminary results need more experimental confirmation.

2.10. The Fluorescence Spectra of Benzine Derivatives

The lifetime of excited molecules and, in particular, those containing a benzene ring, may be studied by fluorescent spectroscopy. In this connection, very valuable information relevant to the effect being discussed here may be obtained from the very interesting works [16] of C. Parmenter and B. Stone and from the more recent ones of D. Nesbit and R. Field. [17] We can evaluate from these papers not only the energy fluctua-

tion lifetime on the benzene ring but also symmetry's influence on it.

Light absorption, as it is known, produces an electronically excited molecule. It can return to its original ground state by relaxation with the emission of radiation (fluorescence). It can be converted also to the ground state of the original molecule by vibrational relaxation that is accompanied naturally by the disappearance of the fluorescence. It enables us to measure the lifetime of the excitation, *i.e.*, the actual lifetime of a vibrational energy fluctuation on a molecule.

The authors studied the transition from the lowest excited singlet (S_1) configuration to the ground state (S_0), *i.e.*, the $S_1 \rightarrow S_0$ fluorescence spectra. They studied such spectra for the symmetrical molecule of p-difluorobenzene (pDFB)

and the molecule of p-fluorotoluene (pFT),
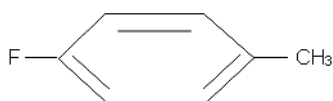
i.e., they studied the result of the symmetry being destroyed by the replacement of fluorine of pDFB with a methyl group.

Thirty of the 39 vibrational degrees of freedom of pFT are in common with pDFB, with almost no frequency change. All of these 30 degrees of freedom relate of course to benzene rings and do not include vibrations of fluorine or the methyl group. The two rings are nearly identical twins, and similar excitations can be produced in each. Thus, the pair provides an opportunity to observe the specific effect of a methyl group on the intramolecular vibrational redistribution (IVR) dynamics of the same benzene rings.

The lifetimes of IVR for S_1 levels of both molecules are presented in [16]. Therefore, for an energy region of 1596 cm^{-1}, the lifetime for S_1 level of pDFB was 290 (a few thousands vibrations) and for pFT only 10 p.s. There is no doubt that the main role in this region is played by the stretch vibrations of the six bonds of the benzene ring whose frequencies are close to this value (presently accepted as 1494 cm^{-1}). It was mentioned above that all these bonds, just as in the benzene ring of pDFB, so also in the benzene ring of pFT, have almost identical frequencies, strengths, and all other properties excepting only one: their inside tensions are somewhat different as a result of influences that are unsymmetrical outward from the rings.

This result emphasizes the very significant role that symmetry plays in the lifetime of the energy fluctuation on a molecule. Really, the full equivalency of the different directions for its flow at a high level of symmetry promotes a higher level of dispersion between these directions. This conforms to the above-mentioned role of the chain branching and other forms of identical bond systems as a fluctuation trap. The very small change in bond strength in the rings leads, in this case, to a quite significant change in internal energy redistribution between the bonds of these rings (~30 times as much). This is consistent with the original supposition on which the effect being considered is based about internal energy redistribution between weak and strong bonds. For, more details of the symmetry's influence see [1].

For the energy region of 1988 cm^{-1}, the lifetime for the S_1 level of pFB was 97 and for pFT ~10 p.s., *i.e.*, the difference between the two rings is lower than for the lower energy region 1596 cm^{-1}. For region 2382 cm^{-1}, the lifetime for S_1 level of pDFB was 25 - 33 and for pFT also 10 p.s. As the region of C-H bond frequencies (2800 - 3100 cm^{-1}) is approached, the differences between the two benzene rings are reduced. This means that the C-H bonds interact with each other more weakly than do the C-C ones and the dispersion of the fluctuation energy through the system of C-H bonds takes place more slowly than through the system of C-C bonds. The C-H bonds can interact only through the C-C bonds, while the C-C bonds interact directly. The energy fluctuation passing through a bonds system with significant frequency changes is hampered, as was also mentioned above.

The general conclusion from these studies is that the benzene ring must be a very effective fluctuation trap. The excited degree of freedom, including the stretching vibration of the C-C bonds of the benzene ring (~1600 cm^{-1}), preserves a few thousand vibrations on it, before it spreads (very slowly) onto other degrees of freedom. This is consistent with the above-mentioned data [1,5], where at least tens of vibrations occur on the ring without any visual indications of an energy transfer to other degree of freedom. This type of the C-C stretch vibration is preserved for the longest time on the benzene ring without mixing with other types. In such a manner, the energy flow through the stretch C-C vibration of the six ring bonds is probably the main factor in the formation of a fluctuation trap. This is the main conclusion. This confirms also the above-mentioned conclusion about weak interaction between systems of C-C and C-H bonds.
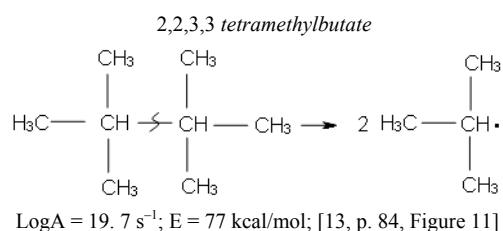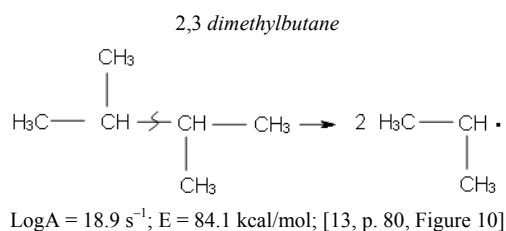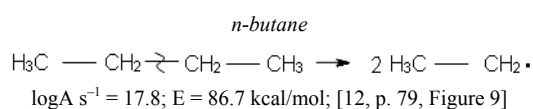
Such results [16,17] go beyond the usual symmetry contribution to fluorescence spectra. The authors rec-

ommend further study of this phenomenon. They write: "The source(s) of the methyl acceleration remains to be established." [16, page 4711].

2.11. The Branching of the Carbon Chain as a Fluctuation Trap in the Bond Fission Reaction

Bond fission reaction (*i.e.*, the initiation reactions in decomposition) has always been of prime interest to kineticists and thermodynamicists. The kinetic study of such a reaction is, as a rule, complicated by the numerous secondary reactions of the produced radicals. One solution is to reduce the reaction time and accordingly the conversion rate, which diminishes the initial radicals' concentration and their secondary reactions. Very low-pressure pyrolysis (VLPP) makes it possible to reduce the conversion time to below 10^{-2} - 10^{-3} second. The VLPP technique is well established as a method for measuring the unimolecular rate constant. The Arrhenius parameters obtained using the VLPP method usually differ somewhat from those received using conventional methods: static or flow techniques. The Arrhenius parameters for this reason must be compared in the framework of the same experimental method, which is important for our analysis. Below are presented Arrhenius parameters of different reactions obtained by the same authors for comparison, using the VLPP method.

The middle bond cleavage in the n-butane, 2,3 dimethyl-butane and 2,2,3,3 tetramethylbutane has been studied for comparison by W. Tsang and J. Kiefer [13]:

n-butane

$$H_3C \longrightarrow CH_2 \overset{\curlyvee}{\longrightarrow} CH_2 \longrightarrow CH_3 \longrightarrow 2\ H_3C \longrightarrow CH_2 \cdot$$

logA s^{-1} = 17.8; E = 86.7 kcal/mol; [12, p. 79, Figure 9]

2,3 *dimethylbutane*

LogA = 18.9 s^{-1}; E = 84.1 kcal/mol; [13, p. 80, Figure 10]

2,2,3,3 *tetramethylbutate*

LogA = 19. 7 s^{-1}; E = 77 kcal/mol; [13, p. 84, Figure 11]

The experimental part of this work using the shock tube technique (VLPP method) was reported in [12].

Transfer from continuous-chain n-butane to branched-chain 2,3 dimethylbutane increases the logarithm of the A-factor, *i.e.*, increases the vibrational energy quantity detained on the transition state and reaction fragments (two identical radicals). The further increase of the branching rate by transfer to 2,2,3,3 tetramethylbutane also increases the logA value.

It is possible to evaluate very roughly the additional energy quantity remaining on the transition state in these reactions. The number of degrees of freedom for distribution of this additional energy is, of course, quite conditional. Transfer from n-butane to 2,3 dimethylbutane increases the logA by 1.1 units, *i.e.*, the additional energy increases to $2.3 \times 1.1 \cong 2.5$ RT. Setting the number of degrees of freedom for 2,3 dimethylbutate as 15 this gives ~ 0.17 RT per each degree of freedom. A similar evaluation gives a value of ~0,2 RT for transfer from n-butane to 2,2,3,3 tetramethylbutane.

For esters pyrolyses this tendency can be seen much more distinctly. The general vibrational energy quantity remaining on each degree of freedom is tenths of RT. As known, the opposite process of intramolecular energy mobilization for a bond that is being broken in the fall-off region is accompanied by similar energy values, removed by one degree of freedom (tenths RT).

## 2.12. The Bond Fission Reaction of Neopentane and Its Derivatives

Neopentane is a maximum branched acyclic alkane, which has a possible maximum of four identical bonds at one carbon atom, with high central symmetry.
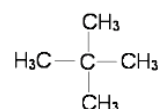
Therefore we can expect a very high rate of energy dispersion inside its molecule at the bond cleavage (demobilization process) and a significant reduction in this dispersion for neopentane derivatives. The one methyl group replacement in neopentane significantly reduces the molecule symmetry as a result, and so also the number of identical bonds for energy dispersion.

It is interesting in this connection to compare the kinetics of the C-CH$_3$ bond cleavage in neopentane and 4,4-dimethylpent-2-yne (DM2P), where one methyl in neopentane is replaced by the acetylenic group [18,19].

logA = 17.3 (s^{-1}); E= 80.8 kcal/mol.

logA = 16.4 (s^{-1}); E = 71.4 kcal/mol.
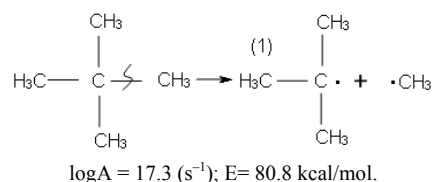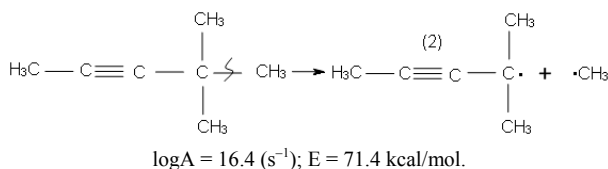
These results are obtained under comparable conditions using VLPP techniques in the particular identical temperature regions, 1000 - 1260˚K for neopentane and 903 - 1246˚K for DM2P,

Vibrational energy flows between similar bonds more easily than between different bonds and also transfers more easily from a strong bond to a weak one than vice versa. Therefore, as a first approximation, it may be assumed that the acetylenic group CH_3-C ≡ C-, which has stronger bonds than C-CH_3, does not participate in activation energy dispersion. In this case, only three C-CH_3 bonds of DM2P participate in the forming of the fluctuation trap, and DM2P has as fluctuation trap of only 9 degrees of freedom, *i.e.*, three degrees of freedom fewer than neopentane.
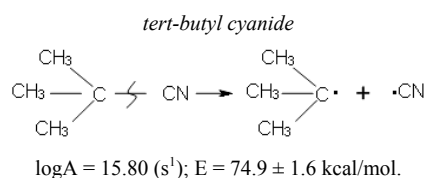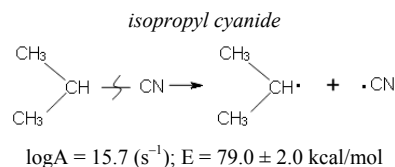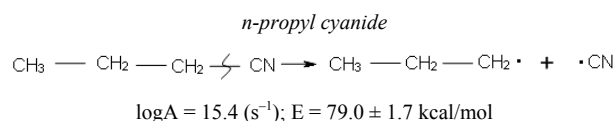
The energy surplus detained on the neopentane molecule at the moment of bond breaking exceeds this value for DM2P by $\Delta logA \times 2.3 \cdot RT = 0.9 \times 2.3 \cdot RT = 2.07 \cdot RT$, that is, it exceeds it by ~ 0.7 · RT per each additional degree of freedom.

The reduction in DM2P's efficiency as a fluctuation trap in comparison with neopentane is obviously connected to the symmetry being destroyed, not only to the fewer numbers of degrees of freedom.

It seems that maximally branched neopentane of the hydrocarbon chain is really a very effective fluctuation trap. If we take into account some contribution of the acetylenic group to energy dispersion, which has been ignored, the energy surplus in neopentane in comparison with DM2P is even increased by values greater than 0.7 · RT per each degree of freedom. Because some energy surplus is detained on the DM2P also, the absolute energy value which neopentane detains on its vibrational degree of freedom may probably exceed a value of one RT.

2.13. The Pyrolysis of n-Propyl Isopropyl and *Tert*-Butyl Cyanides

This was investigated using the VLPP method under the same conditions, in the temperature region 1050 - 1250˚K. [20] The kinetic data of bond fission with · CN radical elimination are as follows:

n-propyl cyanide

logA = 15.4 (s^{-1}); E = 79.0 ± 1.7 kcal/mol

isopropyl cyanide

logA = 15.7 (s^{-1}); E = 79.0 ± 2.0 kcal/mol

tert-butyl cyanide

logA = 15.80 (s^{1}); E = 74.9 ± 1.6 kcal/mol.

Here there is also a clear tendency for the A-factor to increase along with the increase in the carbon chain branching.

The vibrational energy surplus in comparison with n-propyl cyanide, according to expression $\Delta E = 2.3 \cdot \Delta logA \cdot RT$, for isopropyl cyanide equals 0.69 · RT and for t-butyl cyanide to 0.92 respectively, where Δ logA is the difference between the logarithms of A-factors for reactions 2 and 3 and reaction 1. Here the efficiency of isopropyl and t-butyl radicals as a factor that disperses vibrational energy along a molecule is significantly less dominant than, for example, in esters pyrolysis, where these values were 2.3 and 7.36 · RT, respectively. In principle, this may be a result of the reverse strong C≡N bond influence, which leads to the mobilization of vibrational energy for the neighbouring weak C-C bond.

2.14. The Pyrolysis of Tetramethyl and Tetraethyltin

The pyrolysis of tetraalkanes of the IV group of chemical elements, which have a high rate of central symmetry, similar to neopentane's, are accompanied also by high A-factor values, which indicates that a remarkable part of the activation energy is dispersed along the molecule [21,22]. The pyrolysis of tetramethyltin has been studied in a conventional toluene carrier flow system at temperatures from 800 to 940˚K. No appreciable heterogeneous reaction was detected and the first order rate constant appears to have been determined at the high pressure limit [21,22]. No remarkable secondary reactions complicate the main reaction, and the Arrhenius parameters obtained reflect Sn–CH3 bond cleavage
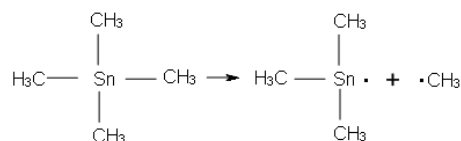

The decomposition of dimethyltindichloride has been

studied in a similar toluene carrier system under comparative conditions. The reaction of Sn-CH$_3$ bond cleavage was first order and homogeneous:

$$\log A = 14.3 \ (s^{-1}); \ E = 58 \ \text{kcal/mol}$$
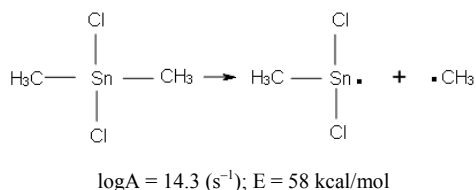
As may be seen, the destruction of the central symmetry of tetramethyltin, with the reduction in the number of identical bonds from 4 to 2, leads to a significant decrease in the logA value by 1.4 units. Here the part of the activation energy dispersed inside the transition state reduces by 2.3·1.4 ≈ 3.2·RT at the transfer from one of the above reactions to another. Here it is very difficult to evaluate this additional energy for tetramethyltin decomposition per one additional degree of freedom. The tetramethyltin has two additional Sn-CH3 bonds, six additional degrees of freedom, in comparison with dimethyltin dichloride, which means a loss of 3.2/6 ~0.5 RT per one degree of freedom. This evaluation must be more if we take into account that here not loss but only substitution of two symmetric bonds for another symmetric one takes place. As above mentioned, this figure for neopentane probably exceeds the value of 0.7 RT. Tetramethyltin, from this point of view, must not differ from neopentane.

In the paper of Johnson and Price [21] there is some rough evaluation of logA values for reactions of successive Sn–CH$_3$ bond cleavage from the following species: Sn(CH$_3$)$_4$; Sn(CH$_3$)$_3$; Sn(CH$_3$)$_2$; SnCH$_3$ down to metallic tin. This evaluation is based on previous studies in their laboratory. They suppose it reasonable to assign the following approximate values to the logA factor: 15.7, 15.0; 14.0; 11.0 (s^{-1}). Albeit these figures are very rough, the general tendency is quite clear: the reduction in the identical bond number at one central atom leads to a significant decrease in A-factor for the reaction of these bonds cleavage. Such a conclusion agrees with our original supposition that a reduction in the identical bonds number at one central atom, i.e., a reduction in branching rate, leads to a decrease in the activation energy surplus remaining on a transition state at these bonds' cleavage.

The replacement of all four methyl groups in the tetramethyltin for ethyl groups leads to an increase of logA-factor from 15.7 to 16.0 for the reaction of this group releases:

$$Sn(C_2H_5)_4 \rightarrow Sn(C_2H_5)_3 + \cdot C_2H_5$$

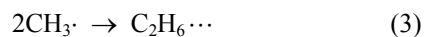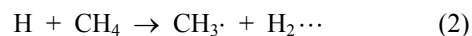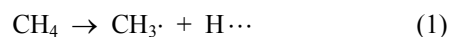$$\log A = 16.0 \ (s^{-1}); \ E = 59.3 \ \text{kcal/mol}$$
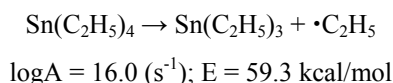
The thermal decomposition of tetraethyltin has been studied under comparative conditions with tetramethyltin in a toluene carrier flow system over the temperature range 725 to 833°K. [22] This A-factor increase is in good agreement with our supposition about the activation energy dispersion between neighbouring identical bonds and groups that are bound with them. Naturally, the complication of identical groups, i.e., their internal energy capacity, must increase the rate of dispersion and accordingly the A-factor. Unfortunately, this A-factor increase is not too large, near to the experimental precision.

The ethyl alkyls pyrolysis of the bivalent metals has been studied under the same conditions [22]. These alkyls have, naturally, a lower degree of symmetry than alkyls of tin with a valency of four. The reaction of bond cleavage with the ethyl group have, according the effect being considered, less lgA-factor than tetraethyltin, which has an logA value of 16.0. The toluene carrier study of diethylmercury gave logA ~ 15.4, and diethylzinc ~14.3. It may be concluded that the substitution in the neopentane of the central carbon atom for other elements of the IV group (Sn, Pb···) changes not very significantly the amount of energy remaining on each degree of freedom.

2.15. The Thermal Decomposition of Methane

It is interesting to consider the influence of the discussed effect on the C-H bond breaking in the example of methane decomposition. The methane has C-H bonds only, which interact one to the other directly, but not through the C-C bonds, which weakens this interaction very significantly. The methane molecule, like the neopentane, has a possible maximum of four identical bonds at one carbon atom, with high central symmetry. Therefore, we can expect, as in the case of neopentane, a very high rate of energy dispersion inside its molecule at the cleavage of one of these four bonds.

The very detailed and careful work of J. Chen and H. Back [23] is a good completion of many previous investigations where unfortunately not all the proper experimental conditions were strictly kept (pressure-dependent region, secondary reaction influence, influence of the deposition of carbon on the surface vessel wall, etc.). It was reasonably concluded in this work that the initial stage of the decomposition (1) can be described by a simple homogeneous, non chain radical mechanism:

$$CH_4 \rightarrow CH_3 \cdot + H \cdots \qquad (1)$$

$$H + CH_4 \rightarrow CH_3 \cdot + H_2 \cdots \qquad (2)$$

$$2CH_3 \cdot \rightarrow C_2H_6 \cdots \qquad (3)$$

In this work, the reaction products hydrogen (2), ethane (3), ethylene, propylene and acetylene were analyzed as a function of time. In the initial stage of the reaction, hydrogen (2) and ethane (3) are the only products that are in equal quantities. The results show clearly that this initial rate of ethane and hydrogen formation is a measure of the initial homogeneous rate of the decomposition of methane, *i.e.*, it is reflected at the primary stage that is of interest to us (1).

In this work, the effect of carbon deposit was negligible; after each experiment its traces were burnt. The influence of the vessel wall is also negligible; the rate of ethane and hydrogen formation in the packed and unpacked vessel was identical. The quartz tube was flushed with hot concentrated nitric acid. The experimental pressure was increased up to the clear entering into the high-pressure region.

The pyrolysis of methane has been studied in a static system at temperature $995 - 1103°K$. The Arrhenius parameters of interest to us at the primary stage (1) of CH_3-H bond cleavage were $\log A(s^{-1}) = 16.45$; $E = 107.6$ kcal/mol. For conventional methods (static and flow systems), and undoubtedly for a simple bond cleavage of the simplest organic molecule, such a value of logarithm A-factor seems too high. The "normal" value in this case probably does not exceed 14.5 - 15.0. The difference between experimental and expected values, 1.5 - 2.00 units ($\Delta \log A$), is equivalent to $2.3 \cdot \Delta \log A \cdot RT$ energy. This additional thermal energy remaining on the methyl radical that is formed is about 0.3 - 0.4 RT per each degree of freedom. An excessive value of activation energy (107.6 kcal/mol), in comparison with the usually accepted C-H bond strength ~98 - 102 kcal/mol, is also in agreement with this conclusion about significant energy remaining on the reaction fragments.

It seems that the energy dispersion rate in methane at its bond cleavage is not significantly different from that in neopentane. Probably, the energy dispersion in the C-H bond system is near to that in the C-C bonds

2.16. The Alkyl Chloride Pyrolysis

The elimination of hydrogen chloride from alkyl chlorides to yield the corresponding olefin proceeds through a four-centered activation complex. This concept is now widely accepted.
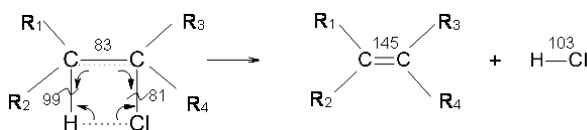
Since in the formation of the four-center transition

state a sizable internal rotation is lost and its structure may be stiffening and strained, an A-factor greater than normal kT/h is not reasonable. Benson and O'Neal [7] estimate a logA-factor on the level of 12.9 - 13.8. They indicate, however, that the experimental values in most cases are significantly higher.

The strengths of all bonds that are being formed and broken in this reaction are indicated on the figure (kcal/mol). In the energized molecule, the energy concentration on the bonds that are being broken (C-Cl and C-H) takes place mainly by energy redistribution inside the transition state ring. These energy flows are indicated on the figure by arrows. The H-Cl bond formation releases 103 and the simple C-C bond conversion into the double bond 62 more kcal/mol. The significant energy flow to the bonds that are being broken (C-H and C-Cl) passes through both the carbon atoms in the ring. Therefore the branching at these carbon atoms (R_1, R_2, R_3, R_4) takes aside a part of energy from these bonds. The lengthening of these radicals increases, naturally, the energy quantity dispersed in such a way and the A-factor value. This influence of the considered effect can quite explain the above mentioned discrepancy between existing theory and experiment that bewildered Benson and O'Neal [7]. They write: "The A-factor appears to increase with the increasing size of the alkyl group in the n-alkylchloride series. Such an effect, if real, is difficult to rationalize" (page 68).

Because of this, in the majority of cases, the authors estimate the Arrhenius parameters as too high and modify them to lower values, in spite of the fact that they state that the rate constants they estimated are reliable. As a preferred value of the A-factor, they accept either the lowest experimental value from among the many results or a value which is lower than them. For example, the experimental value of Arrhenius parameters for pyrolysis of 1-chloro-2-methyl propane are $\log A = 14.0$ and $E = 56.85$ kcal/mol. The authors modify them to the values $\log A = 12.9$ and $E = 53.2$. They write: "Rate constant is reliable but the Arrhenius parameters are probably high" (ibid, p. 69).

The A-factor values estimated by the authors on the base of RRKM are also lower than the experimental data. The empirical Hofmann rule for the direction of esters pyrolysis is similarly explained by the effect being considered here. The branching on the energy flow in the six-centered ring defines this direction (see above).

At the decomposition of cyclobutane derivatives (paragraph 2.5), the main internal energy for bonds breaking arrives from a side chain, but not from the ring. In this case, as distinct from the alkyl chlorides, the length of the continuous side chain promotes energy mobilization.

3. CONCLUSIONS

1) In this article, two types of organic molecule structure are considered, which very often deflect experimental results from those predicted by statistical kinetic theories for unimolecular reaction in the high-pressure region.

a) The structural elements that promote internal energy mobilization accelerate the reaction rate, reduce both the Arrhenius parameters - energy activation and A-factor - and reduce the amount of energy that remains on the reaction fragments.

b) The structural elements that, conversely, impede internal energy mobilization, decrease the reaction rate, and increase both the Arrhenius parameters and the amount of energy remaining on the reaction fragments.

The final dynamic influence depends on the presence in the organic molecule of these two structural elements as much as on the molecular structure between them. The influence of these two structural elements (**a** and **b**) on both Arrhenius parameters is uniform, *i.e.*, it either increases or reduces both of them. Therefore, for the majority of derivatives there exists a positive correlation between energy activation and A-factor. The derivatives whose structure promotes internal energy mobilization are located in the part of the correlation line where both Arrhenius parameters are low, that is, at the lower, left end of the line. The derivatives whose structure impedes internal energy mobilization are located at the right higher end.

2) The breaking of a weak bond in the vicinity of stronger neighbouring ones is accompanied by the reinforcement of the internal energy mobilization of a molecule (type a). The continuous carbon chain neighbouring on this weak bond increases this effect. In this article, this type of influence is considered using as an example the simple bond fission reaction (hydrazine, amine), as is also the ringed transition state reaction (nitroalkanes, orthosilicates, cyclobutanes, and esters). In all these cases, both Arrhenius parameters are significantly lower than predicted by statistical theories.

3) The group of identical bonds that are linked to one another represent the fluctuation energy trap. They promote easy energy circulation inside this group, disperse it between identical bonds and impede its concentration on the bond that is being broken (inside the group or outside it). Such groups include a branched carbon chain as well as a cyclic compound.

4) The influence of the branching is increased in the row, primary, secondary, tertiary, and neopentane type carbon atom; *i.e.*, with the increase in the quantity of identical bonds number in the branching from one to four. This influence is considered using the examples of thermal decomposition of esters, butanes, neopentane

and its derivatives, tetramethyl and tetraethyltin, alkyl chlorides, and methane. In all these cases, the Arrhenius parameters are significantly higher than those expected based on statistical theories. The energy that remains on the reaction fragments, by an order of magnitude, is tenths of an RT per one degree of freedom; it grows with the increase in the branching rate and at its maximum (neopentane) probably approaches the value of one RT.

5) As a cyclic compound, the aromatic substances are considered using toluene, nitrosobenzene, p-diflourobenzene, p-fluorotoluene as an example. The benzene ring is an effective fluctuation trap, dispersing energy mainly through the stretch vibrations of the six identical bonds (type b). The excited degrees of freedom, including the stretching vibration on the C-C bond of the benzene ring, are preserved on these degrees of freedom up to thousands of vibrations without a noticeable spread on the other vibrational mode.

6) The dynamic influence in the esters almost completely fades away during transfer though the carboxyl group from the carbon chain of the alcohol part of a molecule to the acid part, or in the opposite direction. This is a result of the significant difference between the parameters of the bonds of the carboxyl group and carbon chain.

7) The correlation between energy activation and A-factor for the thermal decomposition of cyclobutanes and esters derivatives is considered. Except for the dynamic effect discussed in this paper, which is the basis for the positive correlation for most of the derivatives, the row of other factors influence both the Arrhenius parameters. This leads to some deviation from the correlation line. In spite of this deviation, the positive correlation between two Arrhenius parameters for these two types of derivatives is quite clearly observable; the slope of the correlation line corresponds to the theoretical values for the effect being discussed, the derivatives with structural elements, which promote internal energy mobilization being located in the region of the low Arrhenius parameters at the left lower end of the line, and those which impede this mobilization at the right higher end. The significant deviation from the correlation line is even quite informative, because, in particular, it corresponds to the change in the reaction mechanism, which demonstrates the orthosilicate decomposition.

8) The dynamic interaction between systems of C-H and C-C bonds is considered using cyclobutanes, esters and aromatic compounds as examples. This interaction is much impeded as a result of the significant difference between the parameters of C-C and C-H bonds. Therefore, the C-H bonds' influence on the dynamic picture of an organic molecule, as a first approximation, may be ignored. At the same time, the deutering of the C-H bonds brings their properties a little closer to those of the C-C

ones and other organic bonds, and the influence of C-D bonds becomes more noticeable. The deutering of the organic compounds shift them along the correlation line.

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