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Quantum-Chemical Calculation of the Effect of Stress upon Reactions in Polymers

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The change of energy barrier of stretched model molecules is calculated using semi-empirical quantum-chemical method MNDO. The reactions studied include hydrogen abstraction from polyolefin chains and hydrolysis of polyamide and polyester molecules. Susceptibility of reactions to strain is evaluated. Comparison of calculated results with published experimental data on reactivity of stressed polymers shows that semi-empirical calculations provide reasonable evaluation of stress influence on kinetics of polymer reactions.

KEY WORDS Hydrolysis, ozone, stressed polymers, reactivity, quantum calculation.

INTRODUCTION

It is known that mechanical loading of polymeric materials enhances their reactivity in different types of chemical reactions: ozone oxidation,^{1–5} hydrolysis.^{6–8} Fracture can also be considered as a special type of chemical reaction, which is dramatically affected by the stress.⁹ The qualitative explanation of the influence of stress upon reactivity of polymers is given in References 1–3: in the stretched polymer molecule, geometry and its electronic structure can approach that of the transitional state of reaction, hence the stress promotes this particular elementary reaction. Semi-qualitative analysis of this explanation, that was performed for the reaction of hydrogen abstraction from the polymer chain with cycloparaffines as a reference model for stressed polymers,¹⁰ showed that this explanation is consistent with experiment. This problem, as well as some experimental data, was discussed in detail elsewhere.^{11,12} On the other hand, some attempts were made to evaluate effect of stress upon polymer reactivity using quantum-chemical calculations of the deformed molecules characteristics^{13,14} that are then related to reactivity. (The calculations were based on “second principles” as semi-empiric methods of quantum chemistry only proved to be practical for the task.) Unfortunately, these calculations provide only indirect, qualitative explanation for the reactivity change under stress. Authors of Reference 13 calculated the change of charge distribution in deformed model molecule $H_6Si_2O_7$ and used the change of the charge on nuclei

as a measure of reactivity in some bimolecular reactions of Si—O bond destruction. The calculations of ionization potential change in methane molecule with deformation of valent angle and bond lengths¹⁴ were used in order to explain the formation of charge in fractured polymers.

In the present work we use semi-empiric quantum-chemical calculation to evaluate directly the change in activation barrier of the particular reactions under the deformation of model molecules.

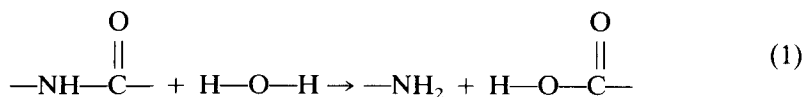
Some preliminary results of this study have already been published in References 15–17.

METHODS OF CALCULATION

Problems of reactions in deformed solids involve at least dozens of nuclei and are therefore beyond the scope of even the most advanced *ab initio* computational methods. We used the semi-empirical MNDO method (Modified Neglect of Differential Overlap)¹⁸ which is known to yield reasonably good results for geometry and formation enthalpy of organic substances.

Molecules analogous in structure to fragments of polymer chains were considered. Methane, propane, isobutane, heptane (in *trans*-zigzag conformation) were used as the model fragments for polyethylene (PE) and polypropylene (PP) chains. Ozone and methyl radicals were chosen as acceptors of hydrogen in the reactions of hydrogen abstraction from polymer chain.

Hydrolysis reactions of polyamide and polyester molecules were studied for the protonated forms of the model molecules. The reasons for this choice of a model were following: i) the very first trial calculations for the reaction of amide bond reaction hydrolysis



have shown that this reaction had a very complicated potential surface map, the reaction path in many-dimensional space of nuclei coordinates being a curve corresponding to concerted motions of several atoms; a search for the true reaction path in the presence of many *cul de sac's* at best becomes a very time consuming task; ii) in the experiment we usually encounter mainly catalytic reactions: reaction is catalyzed by acidic groups that are present in polymer; in environmental aging of polymer carbon dioxide, whatever weak acid it is, provides acidity sufficient for the catalysis; iii) MNDO method, we used in our calculations, is known¹⁹ to poorly represent a hydrogen bond which is present in the initial state for the reaction (1); (one should notice that reasons i) and ii) are closely related.)

The above argument holds for the ester bond hydrolysis. Therefore hydrolysis reactions of protonated forms of ($\text{—NH}_2^+\text{—CO—}$) and ($\text{—OH}^+\text{—CO—}$) were studied.

We used ion $\text{H—NH}_2^+\text{—CO—H}$ (*cis*- and *trans*-conformers) to model polyamide

chain hydrolysis, as well as a longer model—ion $C_3H_7-NH_2^+-CO-C_2H_5$ in *trans*-zigzag conformation. CH_3-OH^+-CO-H (*cis*- and *trans*-conformers) and $C_2H_5-OH^+-CO-CH_3$ (also *cis*- and *trans*-) were used to represent a polyester chain in the hydrolysis reaction. The model molecules of different lengths were used for both reactions in order to judge whether a reaction fragment studied is representative of the polymer chain, i.e. whether the reaction characteristics are independent of the chain length.

The strain of polymer molecule ϵ has been modeled by specifying the distance L between end carbon atoms of model reactional molecule being different from the equilibrium distance L_0 . For the short model molecules, where the hydrogen atom is close to the amide or ester group (and for methane molecule, in the course of hydrogen abstraction modeling) the reactional fragment length L was measured from this hydrogen atom. All other atom coordinates were varied to minimize the overall energy of reactional complex.

For a hydrogen abstraction reaction the H . . . O distance (R) in C—H . . . O—O—O complex or the distance C—H . . . CH₃ have been chosen as a reaction coordinate. A section of a potential energy surface $U(R, L)$ at given value of L was obtained by successive diminishing of the distance R , till the saddle point was reached. In the vicinity of the saddle point the energy U had a stationary value and the distance C . . . H started to increase rapidly when R exceeded the value corresponding to the saddle point.

The reaction path for the hydrolysis reaction: the water hydrogen attacking heteroatom (N or O) adjacent to the carbonyl group, was chosen by minimizing the activation barrier E_a . Another path that could also be imagined, namely, water oxygen attacking carbon atom of carbonyl group, was shown not to lead to the reaction. The calculation of the energy surface for the hydrolysis reaction was analogous to that for the hydrogen abstraction reaction. For free molecule the value of reaction coordinate, i.e. the distance of water hydrogen to heteroatom (N or O) in the molecule backbone R , was successively reduced. For every fixed value of R , all other atomic coordinates were varied to obtain conditional minimum of energy $U(R)$. The calculation proceeded till the saddle point was reached. For the reaction of deformed molecules calculation was performed for either fixed value of the reactive fragment L and successive diminishing of R till the barrier top is reached or vice versa—at constant value of R , the reactive fragment length L was successively increased until the amide (ester) bond rupture. It should be stressed that for this process the reaction coordinate is in fact some curve in multidimensional space of atomic coordinates but, the fact that it turned out to be monotonic in both R and L , makes it possible to use the R or L parameterization of the potential energy surface for the calculation of reaction path.

Semi-empiric quantum-chemical methods should be used with some definite caution in order to avoid slipping into the region of parameters, where the method fails. The MNDO method we used is known to yield reasonably good results for molecular geometry and for the relative change of energy in a series of analogous compounds. As for the absolute values of energies, they are less reliable. Stress induced change of the activation energy ΔE_a should be more accurately predicted since it is change of value in a series of substances that are chemically identical

and differ in their geometry only. The parameterization misfits, that are common for deformed and undeformed states of the molecule, mutually compensate and do not affect energy change under strain. It should also be noted that our calculations have been carried out for isolated molecules, i.e. for the reactions in gas. Use of these calculations to explain the effects characteristic for the solid-state reactions is justified by the very same argument: we evaluate not the absolute energy values but their change under strain. Consequently, we make similar errors for deformed and free molecule when bringing it from solid to gas and these errors should mutually compensate.

DEFORMATION OF MOLECULES

First we tested our analysis of model molecules behavior under strain by studying their deformation. MNDO calculated strain energy dependences $U(\epsilon)$ for propane and heptane molecules are presented in Figure 1 ($\epsilon = (L - L_0)/L_0$ being the strain of a molecule). The calculated values for the ionization potential are also presented. Ionization potential is decreasing with the strain. This may be one of the reasons for the formation of charged particles in polymers under stress (see also Reference 9).

The parabolic dependence of deformation energy upon strain (Hook's law on the molecular scale) holds up to relatively high deformations. The relative role of different deformation modes can be compared when we consider the geometry of the strained molecule. E.g. under 5.8% elongation of a heptane molecule, valent angles at the middle carbon atom change from 112° to 120° , while carbon-carbon bond length changes from 1.542 to 1.575 Å. It means that relative shares of valent

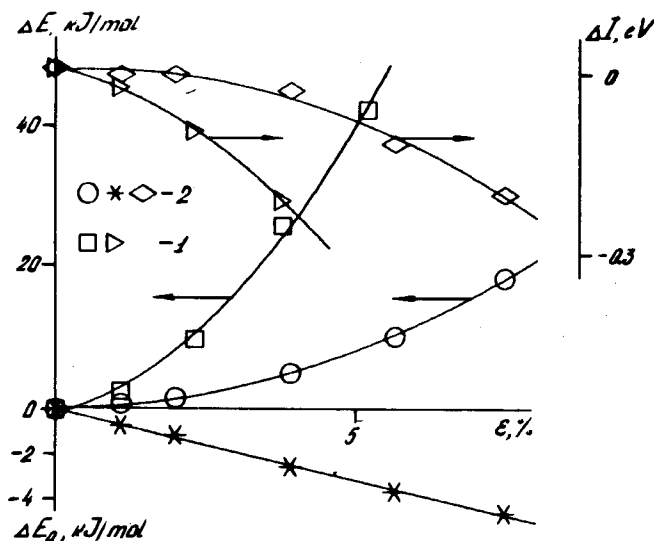


FIGURE 1 Change of activation energy, enthalpy of formation and ionization potential as functions of deformation ϵ . Calculated values for heptane (1) and propane (2).

angles and bond lengths deformation in overall elongation of the chain are comparable—3.7% and 2.1%, respectively.

From the dependences $U(\epsilon)$ we calculated chain stiffness per unit length of the molecule (α/L). For propane molecule the resulting value $\alpha/L = 2.20 \times 10^{16}$ N/mol, for heptane $\alpha/L = 2.82 \times 10^{16}$ N/mol. These values do not differ dramatically and the observed difference is due to the chain end effect of the model molecule. The stiffness for heptane molecule corresponds to Young modulus value 257 GPa (cross-section per molecule in the crystal being 1.8×10^{-19} m²), while experimental value of the crystalline PE modulus is 250 GPa.²⁰ This result is in accord with our computed value.

Stiffness of polyamide chain model molecules determined for the longer model molecule was found to be equal $\alpha/L = 2.90 \times 10^{16}$ N/mol. (Shorter molecules are not representative in this case because C—H, not C—C bonds are stretched in them.) The calculated chain stiffness corresponds to the crystalline Young modulus $E = \alpha/S = \alpha\rho\lambda/m = 260$ GPa. (S being a cross-sectional area per chain, ρ = crystalline density, m and λ = mass and length of the monomer unit). The calculated value for the modulus of trans-zigzag linear crystal is an order of magnitude greater than experimental value for PA-6 reported in Reference 20 and is close to the PE modulus. This discrepancy is presumably due to the presence of folded chains and other softening defects in real PA crystals studied in Reference 20. Other experimental measurements give modulus values much closer to ours (see Reference 21). One can expect, that stiffness of PA-6 molecule shouldn't differ dramatically from that of PE because it consists basically of the same alternating —CH₂— units and stiff amide groups.

For polyester model molecules, linear stiffness values comprise $\alpha/L_0 = 2.03 \times 10^{16}$ N/mol for *trans*-conformer and $\alpha/L_0 = 1.64 \times 10^{16}$ N/mol for *cis*-conformer. Corresponding modulus values are 165 and 133 GPa, respectively. Calculated values are greater (roughly twofold) than the experimentally measured one.²⁰ It should also be noted that, contrary to widely accepted viewpoint the stiffness of *cis*-conformer is close to that of *trans*-conformer. What differs dramatically, is the limit for the linear behavior of *cis*-conformer deformation: whilst *trans*-form elongates linearly over the whole range of deformations studied, ($\epsilon \leq 10\%$), *cis*-conformer deviates from linearity at deformations about 1%.

REACTION OF HYDROGEN ABSTRACTION

Transitional state of the reaction of hydrogen abstraction by ozone is, in fact, a mixture of molecular closed orbital states and a biradical state. As MNDO method gives poor results for biradical states the results of the calculation should be used with some precaution. As a test for calculations validity we used a comparison of the calculated activation energy with experimentally measured values for the reaction of ozone with cycloparaffins. It has been shown previously^{4,10} that cycloparaffins can serve as an experimental model to describe stressed polymer molecules, as their molecular geometry deviates from the optimal for linear molecule and bond lengths and valent angles are deformed as if an external force is applied.

We considered the calculated values of activation energy in different cycloparaffins and corresponding experimental values.

Test calculation was performed for a reaction of hydrogen abstraction by ozone from cyclopropane, propane, and cycloheptane molecules. These molecules served as models for a compressed, a free and a stretched polymer molecule, respectively.

Transitional state geometry turned out to be close to that proposed in Reference 22. Activated complex C—H—O is linear, while H—O—O angle is 116° . Calculated value of activation barrier for propane $E_a = 266$ kJ/mol is fivefold greater than experimentally observed one. For cyclopropane, intramolecular stress results in enhanced C—H bond strength. Hence saddle point is shifted closer to the final products of the reaction. For instance, R_{OH}^* , the saddle point coordinate is 1.03 \AA for propane and $R_{OH}^* = 0.98 \text{ \AA}$ for cyclopropane. The activation barrier for the reaction of cyclopropane is 317 kJ/mol. Hence, relative barrier change is $\Delta E_a = 52$ kJ/mol. Experimentally observed change of reactivity²² corresponds to barrier change of 54 kJ/mol.

For a cycloheptane molecule no straightforward comparison of calculation with experiment can be made, because in cycloheptane molecule different hydrogen atoms are positionally inequivalent and hence differ in their reactivity. Different conformers of cycloheptane molecule enter the reaction simultaneously. Therefore experimental measurements for the cycloheptane oxidation reaction can only yield some mean value for the elementary reactions of different hydrogen atoms abstraction from various conformers. We performed the calculations for cycloheptane in the "armchair" conformation (see Figure 2), which is lowest in energy. C—C—C valent angles in this conformation vary from 116.2° to 119.9° , C—H bond lengths vary from 1.113 to 1.118 \AA . Calculation was performed for four atoms with different initial bond lengths and valent angles at the atom they were attached to. The resulting change of activation energy varied from $\Delta E_a = +8.4$ kJ/mol to $\Delta E_a = -3.3$ kJ/mol. The last one is close to value -6.9 kJ/mol estimated from experimental data.²²

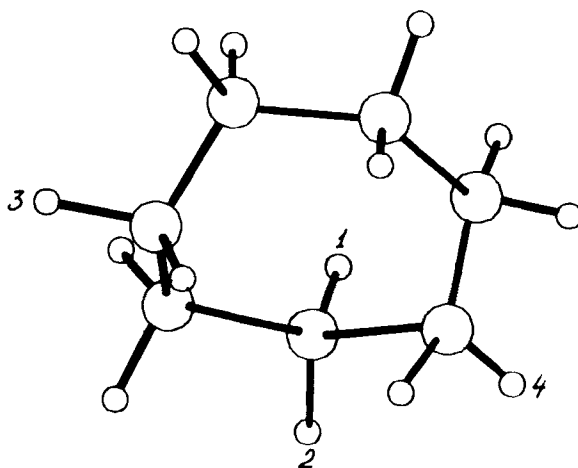


FIGURE 2 Cycloheptane molecule in the armchair conformation. The labelled hydrogen atoms (1–4) are the ones for which the abstraction energy was calculated.

A test calculation for ΔE_a in the hydrogen abstraction by methyl radical was performed for propane molecule and for cyclopropane. As in the case of ozone abstraction, the calculated value $\Delta E_a = 14.2$ kJ/mol was in the range of the estimated ones (we obtained the value $\Delta E_a = 12-14$ kJ/mol from the experimental data^{22,23} supposing that all changes of the rate constants were due to the change of activation energy), whilst the absolute value of the barrier $E_a = 123$ kJ/mol was more than threefold greater than experimentally observed one (35 kJ/mol²²).

From the above consideration it follows that MNDO calculation can provide reasonable results as far as evaluating of ΔE_a is concerned. Calculated ΔE_a values for model cyclocompounds reproduce the sign of the effect and provide, at least approximate value for the change of barrier in stressed molecules. Thus, it is possible to rely upon calculation as a predictive tool for modeling of the reactivity of stretched polymer molecules.

Results of calculations for strained molecules are presented in Table I. The calculation for the change of heptane molecule geometry in the reaction of hydrogen abstraction from the middle carbon atom have shown that length of C—C—C fragment does not change in the course of reaction for both stretched molecule ($L = 8.25$ Å) and the free one ($L_0 = 7.80$ Å). (Results of this calculation are not included in Table I). This result means that the stiffness of the initial molecule and that of the transitional state are close to one another. In order to test the validity of this suggestion we performed the direct calculation for the middle radicals stiffness (propyl, pentyl, and heptyl radicals). The values of stiffness obtained were very close to each other and equal $\alpha/L = 2.5 \times 10^{16}$ N/mol. The latter value practically coincides with corresponding value for heptane molecule.

The geometry of transitional state is not disturbed, as compared with the initial

TABLE I

Reaction	Initial state parameters			Transitional state parameters				ΔE_a
	L	ϵ	ΔH°	R_{CH}^*	$R_{HO(HC)}^*$	L^*	ΔH^*	
	Å	%	kJ/mol	Å		kJ/mol		
$CH_4 + O_3$	*1.80	0	152.9	1.65	0.99	1.85	459.4	306.5
	1.90	5.3	156.7	1.55	0.99	1.90	460.4	303.7
	1.95	8.1	161.8	1.57	1.00	1.95	463.3	301.5
	2.00	11	168.9	1.61	1.01	2.00	464.4	295.5
$C_3H_8 + O_3$	*2.59	0	98.8	1.65	1.03	2.62	364.5	265.8
	2.64	2.0	100.0	1.57	1.03	2.64	364.7	264.7
	2.70	4.1	103.6	1.58	1.04	2.70	367.2	263.6
	2.75	6.1	109.4	1.60	1.04	2.75	372.3	262.8
	2.80	8.1	117.4	1.65	1.04	2.80	379.7	262.3
$t-C_4H_{10} + O_3$	*2.56	0	91.0	1.61	1.06	2.58	342.4	251.4
	2.65	3.4	94.3	1.63	1.06	2.65	344.3	250.0
	2.72	6.1	101.5	1.60	1.06	2.72	351.0	249.5
	2.80	9.2	114.4	1.60	1.07	2.80	363.2	248.8
$C_3H_8 + CH_3$	*2.59	0	3.8	1.36	1.36	2.62	126.9	123.1
	2.80	8.1	22.5	1.31	1.38	2.80	144.8	122.3

* - reaction with free ends of the molecule

molecule, outside the reacting C—C—C fragment. Therefore propane molecule can serve as a representative model for modeling deformation influence on the reactivity of the chain and there is no need in performing time-consuming calculations for longer molecules.

One can see from Table I that stretching of the chain leads to weakening of C—H bonds. As a result, the saddle point moves along the reaction coordinate closer to initial state (greater R). Transitional state energy U^* for the stretched molecule grows with deformation weaker, than the energy of initial molecule U^0 and the activation energy $E_a = U^* - U^0$ drops. Value of E_a depends on deformation almost linearly up to deformation $\epsilon < 8\%$. This dependence is shown in Figure 1.

For same value of deformation the change of activation energy under strain is different for the abstraction of the primary and the tertiary hydrogen atoms. At $\epsilon = 8\%$ $\Delta E_a = -5$ kJ/mol for the primary atom whilst it is -2 kJ/mol for the tertiary one. Substitution of ozone with the more active acceptor, methyl radical, decreases this effect. At the same deformation ($\epsilon = 8\%$) of propane molecule $\Delta E_a = -3.5$ kJ/mol for ozone while for methyl radical only $\Delta E_a = -0.7$ kJ/mol.

Calculations showed unambiguously that stretching of hydrocarbon molecule reduces the potential barrier of the hydrogen abstraction reaction. The strain susceptibility of the reaction rises with the increase of the bond strength and decreases with growing acceptor activity.

The calculated dependence $E_a(\epsilon)$ at small deformation ($\epsilon < 5\%$) is qualitatively the same as the experimentally observed one. More direct comparison of the results of calculation with experiment is possible if we consider reaction under the conditions of constant force rather than under the constant strain as we did.

One can notice that our calculation does not take into account the change in the course of reaction of the zero oscillations energy. For a large molecule with the great number of vibrational modes, the zero oscillations energy can take a large value. It is therefore reasonable to suppose that the change of the vibrational frequencies under the stress overweighs the change of the barrier observed in our calculations. The answers to this question have been partially obtained above: the calculations have shown that no change in the molecular structure was observed in the course of hydrogen abstraction outside the one C—C—C segment. So, the zero oscillations energy is basically the same for the initial (strained) molecule and for the transitional state. Only limited number of oscillational modes related to the reaction fragment can contribute to ΔE_a . This contribution can be evaluated by using IR spectroscopy data. As measured in Reference 24, maximal frequency shift under stress $\Delta\nu$ is not more then 10 cm^{-1} , this value corresponding to the change of the zero energy of reaction fragment less then 0.1 kJ/mol.

HYDROLYSIS REACTION

Calculations for the reaction of acid catalyzed hydrolysis of amides and esters were performed, basically, in the same way as for the hydrogen abstraction reaction. In Figure 3 calculated values of formation energy ΔH of the protonated forms of

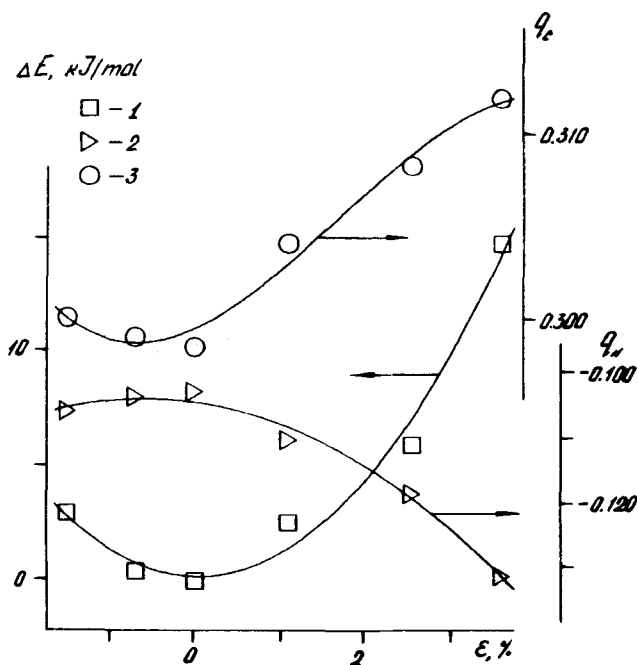


FIGURE 3 Deformation energy (1), charge on atoms N (1) and C (2) of the amide group in $C_3H_7NH_2COC_2H_5$.

model molecules are given vs strain of the molecule ϵ . Change of the charge on amide group atoms under strain is also represented.

It needs mentioning that strain induced change of charge distribution provides supplementary confirmation for the chosen reaction path: positive charge on the carbonyl group carbon diminishes with the strain. This means that hydrolysis reaction would be hindered by strain if it were occurring via water oxygen attack upon carbonyl carbon atom.

Essential calculation results on the energy maps of reactions of amide bond hydrolysis are summarized in Table II and Figure 4.

In reaction of hydrolysis of a *trans*-conformer potential barrier is decreasing monotonously with the growing strain of the molecule. For *cis*-conformer this relation is more complicated. For small strain ($\epsilon < 2.5\%$) value of E_a diminishes with strain, then it rises and stays almost constant. In this case the reaction dependence upon strain is obscured by the conformational transition induced by the stretching. Reaction path is then transferred from one valley of the potential map to another. Reaction by itself is affected not by any strain but only by those deformations that change the geometry of reactive center.

The calculated values of reaction barrier $E_a = 96$ kJ/mol (both conformers of $H-NH_2-CO-H$); 128 kJ/mol ($C_3H_7-NH_2-CO-C_2H_5$) are close to the activation energy values observed experimentally in polyamide-6 hydrolysis $E_a = 83$ kJ/mol (highly oriented PA-6), 100 kJ/mol (unoriented).⁷

Calculations for the ester hydrolysis show basically the same regularities as observed for amide. Changes of properties of reactional fragment are shown in Figure

TABLE II

Reagent	Initial state			Transitional state			E_a
	L	L_c/N_c	ΔH	L^*	R^*	ΔH^*	
	\AA		kJ/mol	\AA		kJ/mol	
<i>trans</i> - $\text{H-NH}_2^+-\text{CO-H}$	**3.59	2.686	342.3	2.933	1.49	442.7	99.9
	3.70	2.740	346.9	2.946	1.50	441.8	94.9
	3.80	2.808	358.2	2.989	1.56	441.0	82.8
	3.90	2.870	374.5	3.045	1.65	448.1	73.2
<i>cis</i> - $\text{H-NH}_2^+-\text{CO-H}$	2.70	2.625	341.5	2.920	1.50	438.9	97.4
	2.90	2.689	345.	2.940	1.50	441.0	95.7
	*2.95	2.621	338.2	2.982	1.52	449.3	100.7
	3.10	2.621	337.7	3.002	1.55	442.2	104.1
	3.15	2.629	338.6	3.008	1.57	440.6	102.0
$\text{C}_3\text{H}_7\text{NH}_2^+\text{COC}_2\text{H}_5$	7.76	2.654	224.9	2.93	1.63	352.4	127.5
	7.90	2.715	230.3	2.896	1.57	354.0	122.9
	8.10	2.790	241.2	2.931	1.65	352.8	111.6
	8.24	2.841	256.7	2.972	1.75	356.6	99.9
	**7.89	2.715	225.7	2.876	1.50	365.3	139.2

* - *cis*-conformer undergoes transition to twisted form under strain
 ** - free-ends molecule reaction

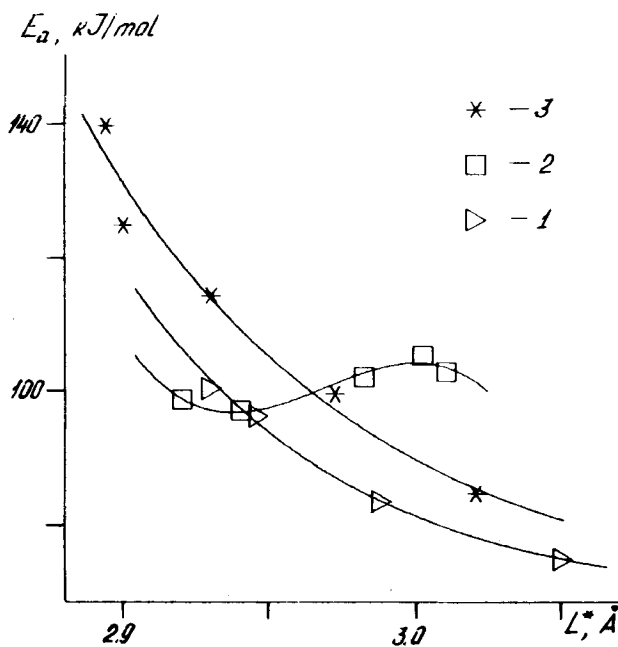


FIGURE 4 Activation energy for the hydrolysis reaction of *cis*- $\text{N}^+\text{H}_3\text{COH}$ (1), *trans*- $\text{N}^+\text{H}_3\text{COH}$ (2) and $\text{C}_3\text{H}_7\text{N}^+\text{H}_2\text{COC}_2\text{H}_5$ (3) dependent upon deformation of reactional fragment.

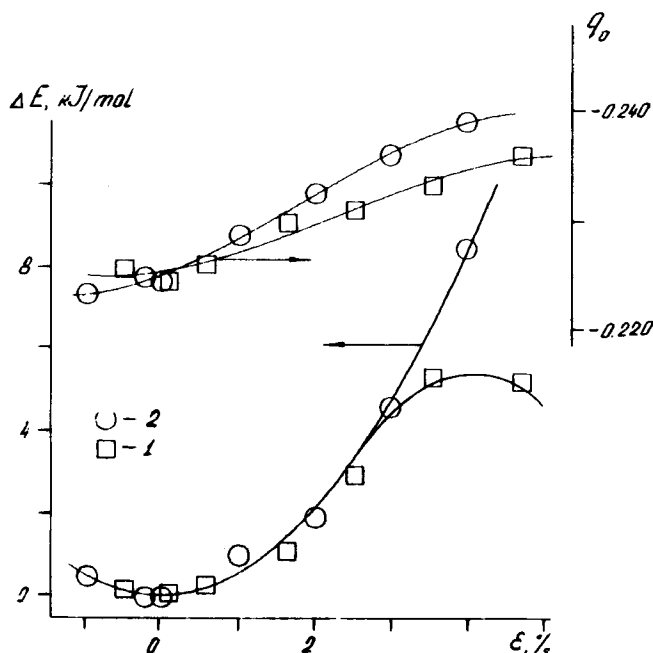


FIGURE 5 Deformation energy, charge on atoms —O— of the ester group and barrier of hydrolysis in $C_2H_5OH+COCH_3$ *cis*-conformer (1) and *trans*-conformer (2).

5. The negative charge on backbone oxygen atom grows under the strain. It makes easier water attack on the ester bond via the reaction path assumed in our calculation (charge on the carbonyl carbon atom does not change in *cis*-conformer and slightly diminishes in *trans*-conformer).



Results of the calculations are summarized in Table III. Shorter reactional fragment appears to be not representative for modeling of polymer reactions. The reactions have strongly differing activation energy for different conformers, whilst for longer fragments this difference is negligible. It should also be noted that the calculated value of barrier for a longer fragment $E_a = 84$ kJ/mol is closer to experimental one.^{25,26}

The calculation of saddle point L^* for this reaction runs into some specific difficulty; the potential surface for this reaction has a very small slope along the barrier. For this reason it makes almost no difference for the reactional system at which particular value of L^* it crosses the barrier. In this case the change in activation energy is primarily due to the rise of the initial state energy under the strain.

DISCUSSION

Calculations performed corresponded to reactions proceeding at a fixed distance between the end atoms of the model molecules. To compare these calculations with reactions in stressed polymers, the force on the reacting segment should be

TABLE III

Reagent	Initial state			Transitional state				E _a
	L		ΔH	L*		R*	ΔH	
	A		kJ/mol	A		kJ/mol		
CH ₃ OH ⁺ COH (<i>trans</i>)	3.50	2.677	222.4	3.534	2.778	1.68	282.2	59.4
CH ₃ OH ⁺ COH (<i>cis</i>)	2.97	2.622	240.4	2.779	2.775	1.68	278.0	54.3
C ₂ H ₅ OH ⁺ COCH ₃ (<i>trans</i>)	4.98	2.673	155.9	-	-	-	-	-
	5.00	2.676	155.9	5.00	2.716	1.78	240.8	84.0
	5.05	2.689	157.2	5.05	2.795	1.79	238.3	81.1
	5.10	2.690	158.0	5.10	2.830	1.81	235.8	77.3
	5.20	2.710	164.7	5.20	2.847	1.85	236.6	71.9
C ₂ H ₅ OH ⁺ COCH ₃ (<i>cis</i>)	4.67	2.688	161.8	4.741	2.804	1.76	247.0	85.3
	4.85	2.732	167.2	4.85	2.846	1.80	243.7	76.5

constant during the reaction rather than its length. Our results can be easily generalized to encompass this reaction mode. To make this generalization we make use of the fact that the energy of the reacting molecule as a function of two arguments, reaction coordinate R and fragment length L in the vicinity of saddle point (R^* , L^*), can be approximated as:

$$U^*(R, L) = A \times (R - R^*)^2 + B \times (R - R^*)(L - L^*) + C \times (L - L^*)^2 + U_0^* \quad (2)$$

The energy of initial state is approximated with Hook's law expression:

$$U^0(L) = D \times (L - L_0)^2 + U_0^0 \quad (3)$$

We determined the values of parameters A , B , C , D , L^* , R^* , L_0 , U_0^0 , U_0^* for each reaction by fitting the entire array of calculated energy values, obtained on the different reaction paths.

In the case of fixed L reactions, the highest energy point is not the saddle point but a point that satisfies the condition $\partial U^*(R, L)/\partial R = 0$. One can easily show that in this case, with an accuracy up to the second order in ϵ , the change in activation energy is:

$$\Delta E_a = K \times (L^* - L_0)^2 - (K/D) \times (L^* - L_0) \times f, \quad (4)$$

where $K = (4AC - B^2)/4C$ and $f =$ force acting on the molecule. In the same manner we can obtain ΔE_a at given constant force on the reacting segment:

$$\Delta E_a = -(L^* - L_0) \times f. \quad (5)$$

Relation (5) is analogous to the experimentally observed one.¹⁻³ If the reaction goes along the path with constant force the susceptibility to stress takes form:

$$\alpha_f = (L^* - L_0) \times S, \quad (6)$$

where S is cross-section per one polymer chain. For constant strain reaction this parameter is:

$$\alpha_e = \alpha_f \times (K/D) \quad (7)$$

The observed experimental value of susceptibility to stress γ (activation volume) is related to α_f via overstress coefficient ψ :

$$\gamma = \psi S(L^* - L_0). \quad (8)$$

One can point that no matter whether the polymer reaction actually proceeds under constant strain of the chain or under constant force applied to the reaction center, its susceptibility to stress is proportional to $(L^* - L_0)$.

The result is quite natural; stretch accelerated reactions which proceed with increasing length of the reaction fragment and vice versa, if the transitional state is shorter than the initial molecule, the reaction is retarded by the stress. Thus, if there exists a possibility to obtain the geometry of transitional state by any simple means (not necessarily such cumbersome method as quantum chemical calculation) it will provide evaluation of reaction susceptibility to stress.

It should also be noted that for the hydrogen abstraction reaction, where no substantial softening of the backbone bonds occurs, α_f and α_e values are close and it is, in fact, not important which particular way reaction follows in experimental sample; whether it proceeds at constant stress or at constant strain, the susceptibility to stress is the same.

As it has been stated above the difference between calculated γ value and the experimental one can be attributed to overstress of molecular chains, that bear the load. Only the most stressed chains are "visible" due to their enhanced reactivity. For polyethylene and polypropylene comparing of calculated γ values with the ones observed experimentally (for the reaction of ozone with oriented PP and PE films $\gamma \approx 9 \text{ cm}^3/\text{mol}^{1-5,10-12}$) yields $\psi \approx 20$, for the reaction of polyamide hydrolysis we obtain $\psi \approx 10$ at draw ratio $\lambda = 3$ and $\psi \approx 6$ at $\lambda = 6$ (the corresponding values of γ are 35 and $20 \text{ cm}^3/\text{mol}^3$). These estimates are well correlated with the known experimental data for overstress of the taut tie polymer chains.²⁷

In Table IV the calculated values of elongation of model molecule during reaction (in other words, susceptibility to stress $L^* - L_0$) are shown. One can see that in series methane-propane-isobutane the susceptibility to stress of hydrogen abstraction by ozone drops. Enhancing of acceptor activity ($\dot{\text{C}}\text{H}_3$ instead of O_3) also affects α_f , the latter being diminished. From above consideration one can conclude that both effects are of the same nature; the closer is the initial state to the transitional one, the less susceptible is the reaction to the external action.

For the reactions of hydrolysis we studied, which involve rupture of backbone

TABLE IV

Reaction	$\alpha, \text{\AA}$
Abstraction:	
methane+O ₃	0.050
propane+ O ₃	0.032
isobuthane+O ₃	0.020
propane+ CH ₃	0.027
Hydrolysis:	
H-NH ₂ ⁺ -CO-H(trans)	0.248
H-NH ₂ ⁺ -CO-H(cis)	0.276
C ₃ H ₇ NH ₂ ⁺ COC ₂ H ₅	0.295
CH ₃ OH ⁺ COH(trans)	0.11
CH ₃ OH ⁺ COH(cis)	0.15
C ₂ H ₅ OH ⁺ COCH ₃ (tr.)	0.17
C ₂ H ₅ OH ⁺ COCH ₃ (cis)	0.19

bonds, the susceptibility to strain is greater than that for reactions of hydrogen abstraction. This result is by no means unexpected; the transitional state formation for hydrolysis reaction implies pronounced elongation of backbone bonds and, therefore, stretching of the reaction fragment facilitates this process.

Direct comparison of the two types of reactions studied runs into difficulties because we deal with two different polymeric materials (PE and PA) and experimentally measured susceptibilities include, of course, structure related factors (cross-section per chain S , overstress factor ψ). This comparison is nevertheless possible if we consider the susceptibilities to stress of two different reactions proceeding in the same polymer. Let us compare the hydrolysis reaction with the reaction of chain rupture. Both these reactions have been studied for polyamide-6 (we suggest here that lifetime of polymeric materials under stress is determined by the kinetics of reaction of chains rupture). The critical value of bond elongation for the backbone C—C bond rupture is not known to authors of this work. However we can use, as an estimate from below, the calculated value of the C—C bond elongation in the transitional state of reaction of middle radical rupture.²⁸ This elongation comprises $L^* - L_0 = 0.6 \div 0.8 \text{ \AA}$. The value is about three times greater than that for hydrolysis reaction. Experimental study of the lifetime of PA-6 films with the draw ratio $\lambda = 6$ yields the value of activation volume for chain scission reaction $\gamma \sim 100 \div 120 \text{ cm}^3/\text{mol}$.²⁴ This value is 3–5 times greater than the activation volume for the reaction of hydrolysis proceeding in the similarly processed films.³ Therefore, the calculated relative susceptibilities of reactions to stress are in good agreement with the experimentally measured ones.

Calculation provides direct confirmation to the above made statement that catalyzed reaction has lower susceptibility to stress than the direct reaction. We performed MNDO calculation of the geometry of C₃H₅—CO—NH—C₃H₅ molecule and its protonated form. The introduction of H⁺ causes C—N bond length growth from the initial value of 1.43 Å to 1.56 Å in protonated form. The elongation of the end-to-end length of the molecule in protonation is also 0.129 Å. The formation

of hydrolysis reaction transitional state implies further elongation of reactional fragment by 0.27 Å. It means that the introduction of proton (acidic catalyst) promotes initial state of the reaction to the transitional state and causes corresponding drop (about 30%) in susceptibility parameter ($L^* - L_0$).

CONCLUSION

The results of our calculation taken together with the known experimental results show that there are some general regularities in stress effect upon kinetics of chemical reactions in polymers. This effect is related to particular type of chemical reactions, polymer structure, and the stress applied. The rate of elementary (as long as one can call solid state reactions elementary) reaction is dependent on stress exponentially, as the main mechanism of stress action upon reactivity is the decrease of the potential barrier due to stress.

All polymer reactions can be classified according to the susceptibility to stress:

1. Reactions that are promoted dramatically under stretching load. These reactions include all the processes which result in rupture of polymer backbone: monomolecular chain scission, middle radical decay, hydrolysis of backbone bonds, etc. The characteristic susceptibility parameter ($L^* - L_0$) of this class of reactions is typically in the range of $0.1 \div 1$ Å (comparable with bond length).

2. Mildly susceptible reactions having ($L^* - L_0$) < 0.1 Å. Hydrogen abstraction reactions with various acceptors are the typical example of these reactions; they proceed at side chemical bonds and do not violate chain integrity though affect geometry of the reactional fragment.

3. Reactions that are not affected with the stress. Any reactions within side groups that do not change a length of macromolecule should not be affected with stretching load. These have ($L^* - L_0$) = 0.

4. Reactions hindered by stress. No matter how absolutely great is shrinkage of the molecule at forming of transitional state ($L^* - L_0$) < 0 these reactions would not be much affected by stretching of polymer. The reason for this low susceptibility is the defective structure of any real polymer sample. The enhanced reactivity of a small fraction of overstressed chains in type 1 and type 2 reactions can be discerned on the background of the low reactivity of the majority of the chains. But one has to suppress the reactivity of the bulk of the molecules to observe the hindered with the stress reactivity. Nevertheless these reactions can be stress affected under loading different from the stretch, e.g. under hydrostatic pressure.

And finally some remarks on application of the concepts we are trying to develop in the present work. First, the application of load can provide us with the tool for selective promoting of chosen elementary stages of complex chemical reactions. Unlike the temperature which promotes all the elementary reactions (though to different extent) stress affects complex reactions much more selectively. Stress effect upon particular elementary reactions in polymers can be precalculated at moderate calculation cost (several Gflop) using state of the art quantum-chemical methods.

Besides, study of stress effect upon polymer reactions provides us with the method

of discrimination of actual elementary reactions involved if detailed reaction mechanism is unknown. We performed this consideration of reaction path for hydrolysis reaction. In order to make discrimination of particular reactions one has to evaluate susceptibility of hypothetical reactions to stress and then to compare it with the actual experimental value.

Summing the results of comparison between our calculations and the experimental values of stress susceptibilities of various polymer reactions, one can claim that the semi-empiric quantum-chemical methods make it possible to evaluate stress susceptibility of different reactions by means of calculations.

References

1. A. A. Popov, B. E. Krisyuk, N. N. Blinov and G. E. Zaikov, *Eur. Polym. J.*, **17**, 169 (1981).
2. A. A. Popov, N. N. Blinov, B. E. Krisyuk and G. E. Zaikov, *Eur. Polym. J.*, **18**, 413 (1982).
3. A. A. Popov, N. N. Blinov, B. E. Krisyuk and G. E. Zaikov, *J. Polym. Sci., Polym. Phys. Ed.*, **B21**, 1017 (1983).
4. A. A. Popov, N. N. Blinov, B. E. Krisyuk and G. E. Zaikov, *Polym. Degrad. and Stab.*, **7**, 33 (1984).
5. B. E. Krisyuk, A. A. Popov and E. T. Denisov, *Vysokomolec. Soedineniya A (Polym. Sci. USSR)*, **30**, 1736 & 1741 (1988).
6. V. A. Bershtein and M. M. Egorova, *Vysokomolec. Soedineniya A (Polym. Sci. USSR)*, **19**, 1260 (1977).
7. B. E. Krisyuk and K. L. Smirnov, *Vysokomolec. Soedineniya A (Polym. Sci. USSR)*, **31**, 328 (1989).
8. B. E. Krisyuk and V. V. Cheremisin, *Vysokomolec. Soedineniya A (Polym. Sci. USSR)*, **34**, no. 11, 93 (1992).
9. G. B. Manelis and E. V. Polianchik, *Sov. Sci. Rev. B. Chem.*, **15**, 61 (1991).
10. B. E. Krisyuk, E. V. Polianchik and A. A. Popov, *Vysokomolec. Soedineniya A (Polym. Sci. USSR)*, **25**, 558 (1983).
11. A. A. Popov and G. E. Zaikov, *J. Macromol. Sci — Rev. Macromol. Chem. Phys.*, **C27**, 343 & 379 (1987–88).
12. A. Popov, N. Rapoport and G. Zaikov, *Oxidation of Stressed Polymers*, Gordon and Breach, New York (1991).
13. T. A. Michalske and B. C. Bunker, *J. Appl. Phys.*, **56**, 2686 (1984).
14. L. S. Zarkhin, K. Ya. Burshtein and N. S. Enikolopyan, *Doklady Akademii Nayk SSSR*, **293**, 133 (1987).
15. B. E. Krisyuk and E. V. Polianchik, *Doklady Akademii Nayk SSSR*, **304**, 1177 (1989).
16. B. E. Krisyuk and E. V. Polianchik, *Khimicheskaya Fizika.*, **9**, 127 (1990).
17. B. E. Krisyuk and E. V. Polianchik, *Khimicheskaya Fizika.*, **12**, 253 (1993).
18. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, **99**, 4899, 4907 (1977).
19. M. J. S. Dewar and H. S. Rzepa, *J. Amer. Chem. Soc.*, **100**, 58 (1978).
20. I. Sakurada, T. Ito and K. Nakamae, *J. Polym. Sci.*, **C**, **15**, 75 (1966).
21. H. H. Kausch, *Polymer Fracture*, Springer-Verlag (1978).
22. A. A. Popov, S. K. Rakovsky, D. M. Shopov and L. V. Ruban, *Izvestiya Akademii Nauk SSSR, seriya chimicheskaya*, 282 (1975); 982 (1976).
23. S. H. Johes and E. Whittle, *Int. J. Chem. Kinetics*, **2**, 479 (1970).
24. R. P. Wool, *J. Polym. Sci., Polym. Phys. Ed.*, **B19**, 449 (1981).
25. R. Colike and L. Lasosky, *J. Phys. Chem.*, **64**, 895 (1960).
26. D. Ravens, *Polymer*, **1**, 375 (1960).
27. V. R. Regel, A. I. Slutsker, E. E. Tomashevskii, *Uspekhi Fizicheskikh Nauk*, **106**, 193 (1972).
28. P. Foster, K. R. Hauschildt and D. Wilhelm, *Macromol., Macromol. Symp.*, **41**, 141 (1991).