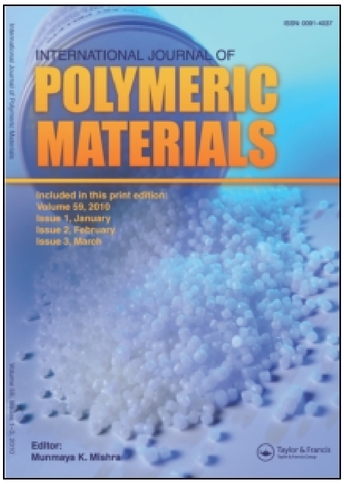

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# Kinetics of Chemical Reactions of Stressed Polymers

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The effect of stress on the rate of chemical reactions is reviewed. It is shown that the sensitivity of the reaction rate to stress depends primarily on two factors; 1) the degree of change in the reactive site geometry, and 2) the energy content of the structural fragment affected by the reaction.

KEY WORDS Stressed polymers, reaction rates, ozonation, polyolefins.

## THEORY AND DISCUSSION

The effect of stress on the rate of chemical reactions of polymers is a problem attracting considerable research activity due to its theoretical and practical importance. Studies by professor H. Kausch[1] have contributed a lot to the present-day understanding of processes taking place in loaded polymers. Related to the problem of polymer strength, durability and chemical stability is the question about the effect of mechanical forces on the reactivity of macrochains.[2] The problem has been further explored in References 3 and 4. Popov[3] explained, from the standpoint of molecular mechanics, the experimentally observed relationship between the rate constant of hydrogen abstraction by ozone ($k$) and the excess stress energy of cycloalkanes ($E_{ex}$):

$$\ln \frac{k_n}{k_6} = \frac{\alpha\sqrt{E_{ex}}}{RT} \tag{1}$$

where $k_n$ and $k_6$ are the rate constants for the compound under investigation and cyclohexane, which was used as a standard, respectively ($n > 6$); $\alpha$ is an empirical constant equal to 57 $(J/\text{mole})^{0.5}$ for the reaction with ozone; $E_{ex}$ is the excess stress energy of the given compound relative to non-stressed cyclohexane. As seen from relationship (1), stretching stress accelerates hydrogen abstraction from the hydrocarbon chain.

Relationship (1) holds for any chemical reaction involving carbon rehybridization from $SP^3$ to $SP^2$ state without ring opening. Even reaction is characterized by a particular $\alpha$ value. The same relationship, but with the opposite sign of $\alpha$, holds for reverse processes ($SP^2 \rightarrow SP^3$) in which case stretching stress decreases the reaction rate.

The above relationship is suitable for describing not only kinetic, but also thermodynamic, effects that is, for quantitatively assessing the effect of structural stress on the position of chemical equilibrium.[3]

The experimentally established dependence of $\ln k_n/k_6$ on $\sqrt{E_{ex}}$ that is, a non-trivial relationship between a parameter characterizing change in reactivity and the square root of that characterizing the energy of the starting molecule, is quite notable. According to the transient state theory, the former should rather be proportional to $\Delta\Delta G^{\neq} = \Delta G^{\neq} - \Delta G_0^{\neq}$ (the difference between the free activation energies of the reaction in question and the standard reaction) or $\Delta\Delta E^{\neq}$ (the difference between the activation energies of the reactions) provided activation entropy is constant or depends linearly on activation energy within the given series of compounds. Such an apparent discrepancy can be explained by analyzing the nature of structural deformation in the compounds under study.

It is known that cycloalkanes with $n > 6$ are characterized by stretching stress due to greater C—C—C valence angles $\varphi$ (116.6° in cyclooctane and 116.1° in cyclodecane) and longer C—C bond distances $l$ (1.536 Å in cyclohexane and 1.545 Å in cyclodecane) and that excess stress energy is largely accounted for by $E_{\text{ang}}$ and $E_{\text{bond}}$ which are proportional to the square of deviations from the optimum values of the respective structural parameters ($E_{\text{ang}} = 0.5 \cdot k_\varphi \cdot (\Delta\varphi)^2$ and $E_{\text{bond}} = 0.5 \cdot k_1 \cdot (\Delta l)^2$, where $k_\varphi$ and $k_1$ are elastic constants).

If the structure of the molecule does not change in the course of the reaction, the components of excess stress energy are to change in the transient state. Thus, $E_{\text{ang}}^{\neq} = 0.5 \cdot k_\varphi (\Delta\varphi - \Delta\varphi^{\neq})^2$. The $\Delta\varphi^{\neq}$ value is constant for each particular reaction and equal to the change in the valence angle on transition from the resting to transient state in the optimal variant: $\Delta\varphi^{\neq} = (\varphi_{0,\text{term}} - - \varphi_{0,\text{init}}) \cdot \delta^{\neq}$, where $\delta^{\neq}$ is the reaction coordinate, $\varphi_{0,\text{term}}$ and $\varphi_{0,\text{init}}$ are optimal values of valence angles in the terminal and initial states, respectively. The contribution of the angle component of excess stress energy to the change in activation energy is equal to $\Delta E_{\text{ang}}^{\neq} = E_{\text{ang}}^{\neq} - E_{\text{ang}} = -\sqrt{2k_\varphi (\Delta\varphi^{\neq})^2 \cdot E_{\text{ang}}} + + 0.5 \cdot k_\varphi \cdot (\Delta\varphi^{\neq})^2$, which demonstrates relatedness of the activation parameter $\Delta E_{\text{ang}}^{\neq}$ to $\sqrt{E_{\text{ang}}}$. There exists also a direct relationship between the full activation parameter $\Delta\Delta E^{\neq} = \Delta E_{ex}^{\neq}$ and the square root of the excess energy of the molecule in the resting state, $\sqrt{E_{ex}}$. Relationship between reactivity and structural stress has the form,

$$\ln \frac{k_n}{k_0} = \frac{\alpha\sqrt{E_{ex}} - B}{RT} \tag{2}$$

where $k$ and $k_0$ are reaction rate constants for stressed molecule with fixed structure and non-stressed one with the optimal structure in the resting and transient states, respectively; $\alpha$ and $B$ are constants for the given reaction. $B$ represents stress energy acquired by a non-stressed molecule on going from the resting to transient state provided the initial structure remains unchanged. It is positive ($B > 0$) and decreases the reaction rate. The parameter $\alpha$ may be either positive or negative depending on the reaction mechanism and deformation type (stretching or compression). It is positive when forces act to change the molecule structure in the same direction in which it changes spontaneously in the course of the reaction that is, when the reaction center undergoes changes which impart it the structure of the transient state and so accelerate the reaction. Otherwise $\alpha$ is negative, and the reaction rate decreases.

The similarity between the experimentally observed relationship (1) and equation (2) indicates that the mechanism by which stress affects reaction kinetics involves influence on the structural parameters of the reaction center in the resting and transient state. The difference between the relationships is due to the fact that in the former case used as a standard is cyclohexane, which has optimal structure only in the resting state, while in the latter it is a molecule with optimal geometry in both resting and transient states.

There is a linear relationship between the parameter $\sqrt{E_{ex}}$ and stress $\sigma$ due to potential energy and stress being related to elastic deformation $K_{el}$ as follows: $E = 0.5\, K_{el} \cdot \varepsilon^2$, $\sigma = K_{el} \cdot \varepsilon$. For the parameter $\sigma$ to be used in equation (1) it should be reduced to one reaction center (a $CH_2$ group).

$$\ln \frac{k_n}{k_6} = \alpha_a \frac{\sqrt{E_{ex}/n}}{RT} \tag{3}$$

where $n$ is the number of carbon atoms in cyclohexane, and $\alpha_a$ for ozone is 5.25 $(kJ/\text{mole})^{0.5}$.

On substituting specific excess stress energy by the equivalent stress-per-bond value, equation (3) assumes the form

$$\ln \frac{k_n}{k_6} = \frac{\gamma_a \sigma}{RT} \tag{4}$$

where $\gamma_a = \alpha_a V \cdot \cos(\varphi/2)\sqrt{2k_y}$ ($V$ is the bond volume and $\varphi$ is the equilibrium value of the valence angle C—C—C).[6,7] The estimated magnitude of $\gamma_a$ for ozone is $2 \cdot 10^{-6}$ m$^3$/mole.

Equation (4) holds not only for model cyclic compounds, but also for the reaction kinetics of non-stressed polymers.[8,9] The only difference is that in the latter case the magnitude of the coefficient of sensitivity to stress $\gamma$ increases by a factor of $\beta$ ($\gamma = \gamma_a \beta$) due to non-uniform distribution of external load between the bonds. The lower limit of $\beta$ is, naturally, unity, which corresponds to the entirely uniform load distribution. Increasing non-uniformity leads to a $\beta$ increase.

The sensitivity of reaction kinetics to stress can be used for studying the supermolecular structure of polymers which determines the degree of non-uniformity in load distribution.

Compare the parameter $\beta$ with the overstress factor $q$ obtained from Zhurkov's durability equation[9]:

$$\tau = \tau_0 \exp\left(\frac{U_0 - q\, V_a \sigma}{RT}\right) \tag{5}$$

where $\tau$ is specimen durability, $\tau_0$ is a pre-exponential factor, $U_0$ is the activation energy of destruction, and $V_a$ is the activation volume of the bond breakage act.

There is a fundamental difference between the parameter $\beta$ and overstress factor $q$. Firstly, time required for evaluating $\beta$ is much shorter than specimen durability $\tau$. Secondly, $\beta$ is determined from the experimentally measured parameter $\gamma_a$ ($\beta = \gamma/\gamma_0$), whereas $q$ is determined using the estimated value $V_a$ ($q = \gamma_\tau/V_a$), where $\gamma_\tau$ is the coefficient of sensitivity to stress in the durability equation) which cannot be measured experimentally and is, for this reason, conventionally assumed to be close to the C—C bond volume.

The first difference is particularly critical when the factors $\beta$ and $q$ are used in studying supermolecular structure. Testing for durability results in that loaded specimens undergo irreversible changes. Therefore, $\gamma_\tau$ and, consequently, $q$ are integral values which depend not only on the initial supermolecular structure, but also on its subsequent changes, accumulated defects, etc. The measurement of $\gamma$, in contrast, requires much shorter exposure of the specimen to load, the minimum measuring time depending on the perfection of the technique used for evaluating kinetic parameters. The maximum shortening of the measuring time is attained using the differential technique which evaluates difference between loaded and non-loaded polymer. In other words, the approach proposed allows the quantitative assessment of the non-uniformity of load distribution between the bonds in the intact specimen, whose supermolecular structure is similar to that of the initial state, and in the specimen that underwent changes on exposure to external chemical, mechanical and thermal factors.

Table I presents $\gamma$ values obtained for oriented polyethylene with high density (HDPE) and polypropylene (PP) in reaction with ozone.

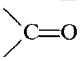
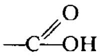
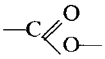
Increasing the temperature results in a more uniform load distribution (smaller $\gamma$), while increasing oxidation level decreases uniformity due, probably, to reduction in the number of passing holding chains in the amorphous phase.

Data on the variation kinetics of factor $\gamma$ could be helpful in designing polymeric products resistant to external factors by varying the supermolecular structure as well as in predicting time-dependent changes in the service properties of materials.

The comparison of $\gamma$ values determined from the accumulation kinetics of various

TABLE I

Coefficient of sensitivity to stress for reaction of oriented polyolefins with ozone

| | Temperature and duration of ozonation | | 20 C° | | 40 C° | 50 C° | |
|---|---|---|---|---|---|---|---|
| | | | 2 hours | 5 hours | 2 hours | 1 hour | 2 hours |
| HDPE<br>λ = 8 | $\cdot 10^6$, $m^3$/mole | | 10.7 | 10.9 | 8.2 | 6.3 | 6.8 |
| | Reaction products | | Radicals |  |  |  |  |
| PP<br>λ = 8 | $\cdot 10^6$, $m^3$/mole, 1 hour | 19°C | 7.8 | 11.1 | 9.0 | 8.6 | 7.9 |
| | | 45°C | — | 9.5 | 8.5 | 5.4 | 4.4 |

functional groups during the ozonation of polymers provides additional information about the reaction mechanism.

Comparing the $\gamma$ value obtained experimentally for the ozonation of oriented specimens of polyethylene with high density and polypropylene with a stretch of $\lambda = 8$ (Table I) and the $\gamma_a$ value for the ozonation of cycloalkanes which is equal to $2 \cdot 10^{-6}$ m$^3$/mole allows the evaluation of $\beta$. In the case under consideration $\beta$ ranges from 3 to 6. The parameter increases with decreasing $\lambda$ so that for polyolefins with $\lambda = 4$ it is as high as 10–15.

Using the parameter $\gamma_a$ all chemical reactions can be divided into sensitive, low-sensitive and high-sensitive with respect to their sensitivity to stress[3] (Table II).

The sensitivity of reaction rate to deformation stress depends, primarily, on two factors. These are the degree of change in the active site geometry in the transient state, which depends on the reaction mechanism and reaction coordinate $\delta^{\neq}$ (the greater the change, the greater the sensitivity), and the energy content of the structural fragment affected by the reaction and directly exposed to the stress (sensitivity grows with energy content). The sign of the sensitivity factor $\gamma_a$ is positive when stress increases and negative when it decreases the rate.

The delimitation of reaction types is not absolute and serves mainly to predict,

TABLE II

Classification of chemical reactions with respect to sensitivity to deformation stress

| Effect of $\sigma$ on reaction kinetics | | |
|---|---|---|
| I. No effect | II. Intermediate effect | III. Strong effect |
| $\gamma_a = 0$ | $0 < \lvert\gamma_a\rvert \leq (0.5 \div 1) \cdot 10^{-29}$ m$^3$ | $\lvert\gamma_a\rvert \geq (0.5 \div 1) \cdot 10^{-29}$ m$^3$ |
| Necessary condition: identical linear dimensions of the reaction center in the direction of the main skeleton in the initial and transient states.<br>The condition is fulfilled for any reaction (any value) provided the reaction site geometry undergoes no changes during the reaction. If the changes do take place, the linear dimension of the reaction center in the initial and transient states can in some cases still coincide. | The fulfillment of one of the following conditions is sufficient:<br>1. The force acts not in the direction of the main change of the reaction center (chemical bond), but in the direction of change of the structural parameter with a smaller energy content (valence and conformation angles).<br>Example: reactions which do not affect interatomic bonds in the main skeleton (ring transformation without opening, polymeranalogous reactions). Absolute $\gamma_a$ values calculated in terms of equation (4) for the most of reactions of cyclic compounds known from literature fall within the interval $(0.21 \pm 0.12) \cdot 10^{-29}$ m$^3$, $\gamma_{a,\min} = 0.02 \cdot 10^{-29}$ m$^3$, $\gamma_{a,\max} = 0.54 \cdot 10^{-29}$ m$^3$.<br>2. Change in the active site geometry is insignificant.<br>3. The reaction coordinate is small. | All of the following conditions must be fulfilled:<br>(i) significant changes in the reaction center geometry;<br>(ii) external force acts in the direction of change in the structural parameter with the highest energy content (bond formation or breakage);<br>(iii) the reaction coordinate is quite large.<br>Example: reactions with the breakage of the main skeleton; data available from literature allow $\gamma_a$ to be estimated as $2 \cdot 10^{-29}$ m$^3$. |

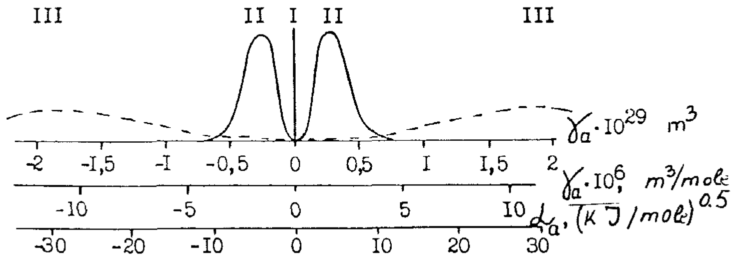


FIGURE 1 Schematic representation of the probability of distribution of chemical reactions in sensitivity to stretching stress (in the case of compressing stress $\gamma_a$ changes the sign).

using the above criteria, the effect of stress on the kinetics of any reaction provided some information about its mechanism is available. It becomes possible to predict the most probable range of $\gamma_a$ magnitudes for any particular reaction. Such a classification holds true for both high- and low-molecular compounds.

The highest sensitivity to stress is, apparently, peculiar to reactions involving bond breakage or formation in the main skeleton [Table II, type III with $\gamma_a \geqslant (0.5 \div 1) \cdot 10^{-29}$ m$^3$]. Less sensitive to load are reactions which do not affect the main skeleton (polymeranalogous reactions and ring transformations without opening, type II). Processes with changes in the chain length may, however, also have low sensitivity to $\sigma$ if their reaction coordinate is small (Figure 1).

The positive and negative parts of range II have been established quite reliably[3] on the basis of a considerable body of evidence on the reactions of monocyclic hydrocarbons. For range III, in contrast, there are only estimates of $\gamma_a$ in the positive region calculated from data on polyamide hydrolysis available from literature,[10] and so range III is depicted in Figure 1 mainly for illustration. From the considerations of symmetry, there should exist the negative part of range III for which no experimental data is presently available. Falling within this range should be reactions involving the formation of new interatomic bonds, such as polycondensation, vulcanization, etc.

Factors that determine reaction rate sensitivity to stress affect also the stress dependence of chemical equilibrium. Therefore, the above classification is likewise applicable to equilibrium thermodynamics. This is confirmed by the fact that $\gamma_a$ values for equilibrium reactions of cyclic compounds fall within range II which is characteristic of reactions without bond breakage in the main skeleton. The approach proposed allows therefore not only qualitative, but also quantitative, prediction of the effect of stress on the equilibrium parameters of the reactions of cyclic and high-molecular compounds.

According to the classification, monomolecular destruction of macromolecules under the action of stretching stress should fall within the positive region of range III. Such a conclusion agrees with the estimate of about $3 \cdot 10^{-29}$ m$^3$[10] for $V_a$ in Zhurkov's equation (5).

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