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Title	Free radical reactions at high pressures (Modern aspects of physical chemistry at high pressure : the 50th commemorative volume)
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Citation	The Review of Physical Chemistry of Japan (1980), 50: 217-229
Issue Date	1980
URL	http://hdl.handle.net/2433/47093
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

FREE RADICAL REACTIONS AT HIGH PRESSURES

By V. M. ZHULIN

In this article the author does not present the complete review of the works concerning free radical reactions at high pressures. He aims at the presentation of the principles, conclusions, and explanations which are the most inetresting from his point of view. Thus the author dwells upon two domains viz. free radical reactions in the liquid phase and solid-phase reactions initiated by shear. These two divisions considerably differ in the amount of experimental data as well as in the level of theoretical development.

The review includes in particular the following points. The rate of radical "cage" reactions may be determined by that of the rotational diffusion and consequently may decrease as the pressure increases. The chain termination in thermal polymerization of styrene seems to proceed in kinetical area because the reaction is characterized by a negative activation volume. There exist quantitative relations between the rate constant and activation volume of the radical substitution reactions involving the transfer of H atom from organic compounds to the free radical. The existence of the relations is stipulated by different lengthening of valence bonds in the transition state. Deformation of organic substances at high pressure gives rise to new chemical and kinetical phenomena which can not be interpreted from the known points of view on high pressure effects.

1. Liquid-Phase Reactions of Free Radicals

Kinetical studies performed at high pressures permit the estimation of activation volumes ($\Delta V^{\neq}$) of the chemical reactions. thus yielding in valuable information on the structure of transition states and the mechanism of the processes. ΔV^* values may be derived from the equation of the theory of the transition state (activated complex)[1,2]

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = -\frac{\Delta V^{\neq}}{RT} \qquad (1)$$

where k is rate constant and ΔV^* change in the volume by formation of 1 mol of activated complex; all concentrations are molal. It yields from Eq. (1) that ΔV^* is a fundamental physico-chemical value; its sign determines the direction of pressure effect ($\Delta V^* < 0$ —acceleration, $\Delta V^{\neq} > 0$ – slowing down) and its absolute value the magnitude of the effect.

The exact determination of ΔV^* from the dependence of $\ln k_p$ vs. P is connected with some difficulties. for the dependence is commonly non linear. Various methods of estimation of $\Delta V^{\neq}$ are used. thus $\Delta V^{\neq}$ value depends not only upon the amount and the accuracy of experimental data but also upon the method of calculation.[3]

1-1. *Homolysis of organic compounds; "cage" effect*

There exist a considerable number of azo and peroxide compounds which are decomposed with the formation of two free radicals one of which rapidly produces N_2 or CO_2 molecule, thus radical recombination in the primary "cage" does not lead to the source compound. In this case the kinetical study of the decomposition at various pressures performed by measuring the concentration of the source material as a function of time enables us to estimate of the activation volume ΔV_i^* which is related to splitting of one of chemical bonds. ΔV^* values for homolysis of azobisisobutyronitrile,[4,5] cis-3, 6-diphenyl-3, 4, 5, 6-tetrahydropyridazine,[6] carbo-tert-butylperoxycylohexane,[7] di-tert-butyl-hyponitrite,[8,9] azocumene, and p, p'-dimethylazocumene[10] were found to be 3-5 cm³/mol. These values seem probable in case of the considered process on base of simple "sterical ideas" presented elsewhere[11] where the author surmises the 10-20% increase in the bond length following the formation of the transition state. However, studies on the decomposition of some other compounds by the same method point to considerably higher ΔV^* values. Thus the study of decomposition of p-nitrophenyl-azotriphenylmethane in n-octane, cumene, and tert-butylbenzene yielded in the ΔV^* values equalling to 18, 20, and 21 cm³/mol respectively.[10] $\Delta V^* > 5$ cm³/mol were also obtained for the decomposition of tert-butylperoxide in various solvents[12] as well as for tert-butyl 2-propyl-2-peroxypentenoate.[13]

The similar results may be derived from kinetical studies of azobisisobutyronitrile, for instance, not by means of the concentration monitoring but using compounds— "radical traps".[4,5,14,15] It is known that the experiments are carried out under conditions which provide "trapping" of the radicals out of the "cage" only. In this case the rate constant (k_i) is a complex function which may be presented as follows

$$k_i = k_d \frac{k_D}{k_C + k_D},$$

(2)

where k_d is rate constant of decompsoition of the compound into the radicals, $k_D/(k_C+k_D) \equiv f$ portion of outer radicals, k_D rate constant of outlet of the radicals from the "cage" (proportionate to diffusion coefficient), the k_C rate constant of radical reaction within the "cage" (recombination or disproportioning).

The separate estimation of k_i and k_d at various pressures permits the evaluation of changes in f under the condition of increasing pressure. According to the experimental data f decreases along with pressure increase, and that means the growth of the portion of therad icals which react within the "cage". These results were for a long time interpreted as follows: the rate of outlet of the radicals from the "cage" should decrease with increasing pressure owing to the increase in viscosity of the medium and the reaction in the "cage" being bimolecular, should be followed by the decrease in the volume by the formation of the transition state, so the reaction rate should grow up with the increasing pressure.

In 1972 another approach was proposed to the consideration of the pressure effect on k_C and k_D.[16] Basing on Eq. (2) we may put down the following expression

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$$\frac{1-f}{f} = \frac{k_C}{k_D} \tag{3}$$

Then

$$-RT\left(\partial \ln\frac{1-f}{f}\Big/\partial P\right)_T = \varDelta V_C^{\pm} - \varDelta V_D^{\pm} \tag{4}$$

where $\varDelta V_C^{\pm}$ and $\varDelta V_D^{\pm}$ are activation volumes of internal radical reaction and disappearance of radicals from the "cage" respectively. It is surmised that $\varDelta V_D^{\pm}$ equals to activation volume of viscous flow of the solvent and may be expressed as follows:

$$\left(\frac{\partial \ln V\eta}{\partial P}\right)_T = \frac{\varDelta V_D^{\pm}}{RT}, \tag{5}[17]$$

where V and η are molar volume and viscosity of the solvent respectively. The compressibility of the liquid is low; therefore, $\varDelta V_D^{\pm}$ is determined by the magnitude of η changes by increasing pressure; these data are available for many solvents. The work[5] presents the experimentally estimated value $\varDelta V_C^{\pm} - \varDelta V_D^{\pm} = -9 \, \text{cm}^3/\text{mol}$ for cyano-iso-propyl radicals, and $\varDelta V_D^{\pm} = 15 \, \text{cm}^3/\text{mol}$ was reported[16] for toluene which was taken as reaction medium. Thus, $\varDelta V_C^{\pm}$ equals $6 \, \text{cm}^3/\text{mol}$ i.e. the radical reaction within the "cage" is inhibited by pressure.

This result was explained[16] by the dependence of the rate of internal reaction upon the rate of their rotational diffusion which is naturally dependent upon the viscosity of the medium. As pointed out above, the ratio k_C/k_D is commonly decreased with the pressure increase; i. e. k_C is less affected by viscosity than k_D is.

The ground for the considered approach to the estimation of k_D and k_C is supported by the series of works by Jonas et al.[18-22] In these works the activation volumes of translational ($\varDelta V_{tr}^{\pm}$) and rotational ($\varDelta V_r^{\pm}$) translocations of molecules (autodiffusion) were estimated on base of NMR data on proton spin-lattice relaxation times. It proves that $\varDelta V_{tr}^{\pm}$ is quite near to $\varDelta V_D^{\pm}$ calculated on base Eq. (5), and that $\varDelta V_r^{\pm} \leqslant \varDelta V_{tr}^{\pm}$. Some results are given in Table 1.

Let ($\varDelta V_C^{\pm} - \varDelta V_D^{\pm}$) be equal to ($\varDelta V_r^{\pm} - \varDelta V_{tr}^{\pm}$), the ($\varDelta V_C^{\pm} - \varDelta V_D^{\pm}$) for the solvents presented in Table 1 may vary from -15 to $0 \, \text{cm}^3/\text{mol}$. It follows that systems principally are possible where k_C/k_D is slightly dependent upon pressure (viscosity) as far as $\varDelta V_C^{\pm} \approx \varDelta V_D^{\pm}$. Though the "cage" effect occurs in these systems it cannot be registered basing on the changes in viscosity of the medium. On the other hand, if homolysis is carried out in solvents like benzene one may expect considerable growth in k_C/k_D with increasing pressure for radical

Table 1. Activation volumes of translational ($\varDelta V_{tr}^{\pm}$) and rotational ($\varDelta V_r^{\pm}$) translocations of molecules in the liquid phase (23°C)

compound	$\varDelta V_{tr}^{\pm}$	$\varDelta V_r^{\pm}$	$\varDelta V_r^{\pm} - \varDelta V_{tr}^{\pm}$	Ref.
benzene	22.0	7.4	−14.6	18
acetone	13.6	4.8	− 8.8	18
toluene-d_3	14.4	10.4	− 4.0	19
chlorobenzene	11.2	11.7	0.5	18

reaction within the "cage" is considerably less inhibited by pressure than the outlet of the radicals (f is strongly decreased by increasing pressure, and $\Delta V_i^{\neq}$ is a great positive value).

Jonas *et al.* relate these phenomena to different connections between translational and rotational translocations of molecules. Rotation of symmetrical molecules has a slight effect on the local structure of a liquid *i.e.* it is less effective in causing translational movements of molecules than rotation of nonsymmetrical molecules. Naturally, all these phenomena were observed by studying autodiffusion processes. In common case the ratio k_C/k_D in free radical reactions may depend on the radical structure as well as on the nature of the solvent used. However, already now these ideas may be applied to the explanation of many experimental results concerning "cage" effect in particular. Thus, the work[12] reports $\Delta V_i^{\neq}$ values obtained by studying decomposition of *tert*-butyl peroxide in benzene, tetrachloromethane, cyclohexene, and toluene equalling to 12.6, 13.2, 6.7, and 5.4 cm³/mol respectively. The presented results show $\Delta V_i^{\neq}$ to be high in the symmetrical solvents while being near to $\Delta V_d^{\neq}(\Delta V_c^{\neq}\approx\Delta V_D^{\neq})$ in nonsymmetrical solvents.

Reference (14) reports the values of $\Delta V_i^{\neq}$ for decomposition of azobisisobutyronitrile at 40°C in toluene (10.7 cm³/mol), methylcyclohexane (17.2 cm³/mol), and cyclohexane (34.9 cm³/mol). Using data[5,14] and $k_d=5.45\times10^{-7}$s⁻¹(40°C) we have calculated $\Delta V_c^{\neq}$ 10 cm³/mol (toluene), 5.9 cm³/mol (methylcyclohexane), and $\sim$0 cm³/mol (cyclohexane). Thus, in the solvent with symmetrical structure (cyclohexane) pressure increase does not affect the radical reaction within the "cage", while the viscosity of cyclohexane increases more than that of the other two solvents, so that $\Delta V_D^{\neq}$ and $\Delta V_i^{\neq}$ give the highest positive values.

It sthould be emphasized that any known result may not be taken clearly from the considered point of view. Thus, for instance, we may point to the results[10] on the decomposition of *p*-nitrophenylazotriphenylmethane in n-octane, cumene, and *tert*-butylbenzene. It can hardly be said that the molecules of these solvents are symmetrical, but $\Delta V_i^{\neq}$ of the decomposition are quite high and practically the same in all these solvents (*ca.* 20 cm³/mol).

Another problem which arises by interpreting experimental data may be shown on the example of the data on the decomposition of *tert*-butylhyponitrite in n-octane[8,9]. $\Delta V_D^{\neq}$ derived from viscosity changes under condition of increasing pressure equals to 21 cm³/mol. (1 atm, graphical differentiation of the dependence "ln $\eta - P$"). The analagues evaluation of $(\Delta V_c^{\neq}-\Delta V_D^{\neq})$ from the dependence "ln $(k_C/k_D)-P$" yields in the value -30 cm³/mol, consequetly $\Delta V_c^{\neq}$ equals to -9 cm³/mol, *i.e.* the reaction of *tert*-butoxy radicals within the "cage" is accelerated by pressure. The estimation of the respective activation volumes at 2000 atm leads to the positive value $\Delta V_c^{\neq}\approx4$ cm³/mol. It is difficult now to point out the real nature of this phenomenon. Perhaps it is bound with the transfer of the reaction into diffusion area from the kinetical one.

Finally we should point out the variety of the kinetical effects of high pressure showed by studies on decomposition of organic peroxides. Here negative $\Delta V^{\neq}$ values were obtained along with positive ones. Reference (23) reports on the acceleration of homolysis of isobu-

tirylperoxide ($\Delta V^* = -5$ cm³/mol). In this case just radical process is considered for the contribution due to the rearrangement which is considered nonhomolytic is quite low. This reservation is made because of some known data[24,25] on the transformation of a number of silicone peroxides for which only rearrangement is known which is accelerated by pressure ($\Delta V^* = -8 \pm 1.5$ cm³/mol[25]; no products of radical decomposition are observed).

In the case of the decomposition of *trans-4-tert*-butylcyclohe xanecarbonyl peroxide the contribution due to the products of homolysis is unclear. However, it is known that the decomposition is accelerated by pressure ($\Delta V^* = -4$ cm³/mol) and that a product of rearragement is formed.[26]

Thermal decomposition of dimethyl ester of peroxydiglutaric acid may be characterised at least by two specific features.[27] The first is that the rate constant of the reaction is independent upon pressure within the wide range (1–10000 am), and the second is connected with the fact that the reaction of radicals within the "cage" is more inhibited by pressure than their outlet.

Finally, by studying the decomposition of benzoyl peroxide in chloroform Walling *et al.*[26] observed both acceleration and inhibition of the reaction by pressure *i.e.* the velocity of the decomposition obtained minimum at 700 atm.

The presented various pressure effects on the decomposition of peroxides cannot be now strictly interpreted. Further experiments are required.

1-2. *Reactions of propagation and termination of chain in radical polymerization*

The common expression for the initial rate of polymerization may be put down as follows

$$W = W_i^{1/2} \frac{k_p}{k_t^{1/2}} [M] \tag{6}$$

where W_i is initiation rate and k_p and k_t are rate constants of propagation and termination of chain, respectively: [M], monomer concentration.

Thus, if W_i is available one may derive the ratio $k_p/k_t^{1/2}$ from the polymerization rate. According to Eq. (6), the dependence "ln W vs. P" enables the estimation of the overall activation volume (ΔV_W^*) which equals to

$$\Delta V_W^* = 1/2 \Delta V_i^* + \Delta V_p^* - 1/2 \Delta V_t^* \tag{7}$$

Consequently the data on the rates of polymerization and initiation do not permit the estimation of the absolute values of k_p and k_t as well as those of ΔV_p^* and ΔV_t^*. This estimation requires some auxiliary method. For the first time the separate estimation of k_p and k_t was carried out for styrene polymerization under chopped light irradiation (30°C). According to the data[28] the propagation of the chain is accelerated ($\Delta V_p^* \approx -13$ cm³/mol), while termination is inhibited ($\Delta V_t^* \approx 16$ cm³/mol) by pressure. Walling and Pellon evaluated k_p at various pressures by emulsion polymerization.[29] Our calculations based on these data yielded in $\Delta V_p^* = -20$ cm³/mol at 1 atm.

The estimations of ΔV_p^* and ΔV_t^* are quite laboured and require a complex apparatus.

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Table 2. Activation volumes $\Delta V_p^{\ddagger}$ and $\Delta V_t^{\ddagger}$ and reaction volume (ΔV_p) of polymerization
of monomers (30°C). cm³/mol

monomer	$\Delta V_p^{\ddagger}$	$\Delta V_p^{a)}$	$\Delta V_t^{\ddagger}$	Ref.
styrene	−17. 9	−18. 1	13. 3	30
methylmethacrylate	−19. 0	−25. 1	25. 0	31
butylmethacrylate	−23. 2	—	17. 8	32
octylmethacrylate	−24. 7	—	20. 8	35
butylacrylate	−22. 5	−19. 9	20. 8	33
vinylacetate	−23. 3	−20. 9	16. 3	34

a) Calculated on base[37]

Therefore. sometimes $\Delta V_p^{\ddagger}$ was taken equal to the change in the volume of the system by
polymerization (ΔV_p). As the recent systematic studies by Japanese investigators showed[30-36]
this supposition is not groundless. It yields from the data presented in Table 2 that $\Delta V_p^{\ddagger}$ is,
apparently, equal to ΔV_p within the limits of experimental errors. The most considerable
disagreement between $\Delta V_p^{\ddagger}$ and ΔV_p is observed for methylmethacrylate.

Polymerization of the monomer is characterized by the highest $\Delta V_t^{\ddagger}$ value. In addition
the dependence ln k_t vs. P may be presented by a curve with a sharp slope in the region
below 500 atm and slightly dependent upon pressure in the range 500-1000 atm. Practically
the main decrease in k_t occurs before 250 atm (k_t undergoes half decrease). Then if the
linear dependence ln k_t-P is accepted in the range 1-250 atm. $\Delta V_t^{\ddagger} \approx 70$ cm³/mol may be
obtained. However, the physical sense of this value is still unclear. Also unexplained is the
nature of considerable disagreement between $\Delta V_t^{\ddagger}$ values reported by Ref. (31) (29. 2 cm³/mol)
and by Ref. (15) (7. 0 cm³/mol). The difference in the experimental techniques is that in
Ref. (31) W_i was determined by the aid of diphenylpycrylhydrazyl in the atmosphere of
nitrogen while in Ref. (15) iminoxyl radical in vacuum was used.

On the whole. from the author's point of view which is supported by the data[36] $\Delta V_t^{\ddagger}$
values are in the first approximation equal to $\Delta V_D^{\ddagger}$ of the monomer derived from the Eq (5).

1-3. On reactions of initiation and termination of chain in thermal (uninitiated) polymerization of styrene

Only two works are known up to the date which aim basically at the estimation of the
activation volume of reaction of initiation in thermal polymerization of styrene.[39,40] Basing
on the data on the velocities of initiated (benzoyl peroxide) and uninitiated polymerization
of styrene and on the values of molecular masses. Guarise[39] estimated the overall activation
volumes of thermal ($\Delta V_{W,th}^{\ddagger} = -25. 8$ cm³/mol) and initiated ($\Delta V_{W,i}^{\ddagger} = -17$ cm³/mol) as that of the
reaction of initiation by benzoyl peroxide ($\Delta V_i^{\ddagger} = 5$ cm³/mol). Then using Eqs. (7') and (7'')

$$\Delta V_{W,i}^{\ddagger} = 1/2\Delta V_i^{\ddagger} + \Delta V_p^{\ddagger} - 1/2\Delta V_t^{\ddagger} \qquad (7')$$

$$\Delta V_{W,th}^{\ddagger} = 1/2\Delta V_{ith}^{\ddagger} + \Delta V_p^{\ddagger} - 1/2\Delta V_t^{\ddagger} \qquad (7'')$$

and accepting $\Delta V_p^{\ddagger}$ and $\Delta V_t^{\ddagger}$ equal for both the processes, Guarise derived from these equations

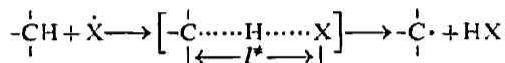(7') and (7'') $\varDelta V_{itA}^{\neq} = -12.6\ \text{cm}^3/\text{mol}$.

In the work[40] $\varDelta V_{itA}^{\neq}$ was estimated using stable iminoxyl radical at $80°$C and the value obtained was equal to $-32\ \text{cm}^3/\text{mol}$. Such a considerable discrepancy may be stipulated by a number of reasons. Both of these methods of estimation of $\varDelta V_{itA}^{\neq}$ are not ideal. Thus, the supposition on the equality of $\varDelta V_i^{\neq}$ for thermal and initiated polymerization of styrene seems apparently groundless (see later). Moreover, the method of the estimation of $\varDelta V_{itA}^{\neq}$ with the aid of stable iminoxyl radicals proved to be indirect, for the radicals are not only involved into reactions with the radicals formed by thermal initiation, but also bind to styrene. However, the value $\varDelta V_{itA}^{\neq} = -32\ \text{cm}^3/\text{mol}$ which is characteristic of the Diels-Alder reaction correlates well with the initiation mechanism proposed by Mayo[41] –two styrene molecules react in Diels-Alders' condensation type forming quite reactive bicyclic compound which donate hydrogen atom to the third styrene molecule, so the process corresponds to the third order of the dependence of the initiation rate upon the monomer concentration. If we accept $\varDelta V_{itA}^{\neq} = -32$ cm^3/mol and use $\varDelta V_W^{\neq} = -32.5\ \text{cm}^3/\text{mol}$[40] and $\varDelta V_f^{\neq} = -21.7\ \text{cm}^3/\text{mol}$ (the value -17.9[30] is extrapolated to $80°$C on base of Ref. (3)) we obtain from the Eq. (7) $\varDelta V_t^{\neq} \approx -10\ \text{cm}^3/\text{mol}$. Thus the reaction of termination of the chain is accelerated by pressure in case of the thermal polymerization of styrene. The given $\varDelta V_p^{\neq}$ and all data reported by Guarise[39] permit the evaluation of $\varDelta V_t^{\neq} = -4\ \text{cm}^3/\text{mol}$ (thermal polymerization) and $\varDelta V_t^{\neq} = -5\ \text{cm}^3/\text{mol}$ (initiated polymerization). These figures are especially competent in case of initiated polymerization, and it can be seen that $\varDelta V_t^{\neq}$ is again negative. It appears that the termination of styrene poly-merization chain is really accelerated by increasing pressure. Perhaps it is bound with the fact that chain termination involves low molecular radicals (arising from thermal initiation) and the reaction proceeds not in diffusion but in kinetical area (contrary to the termination on high molecular radicals).

1-4. Reactions of radical substitution

Studies on the reactions of polymerization and telomerization in the presence of CCl_4 as chain transferer showed that the activation volume in reactions of radical substitution ($\varDelta V_n^{\neq}$) involving transfer of Cl atom is practically independent upon the radical structure and obtains the value near to $\varDelta V_p^{\neq}$.[42] However the consideration of respective reactions involving hydrogen transfer yielded in the existence of the correlation between rate constants of radical substitution and $\varDelta V_n^{\neq}$.[42,43] Later this correlation was estimated for the reactions of hydrogen splitting by $-\overset{|}{\underset{|}{C}}\cdot$,[44,45] Br,[46-49] and $(CH_3)_3 CO$[50] radicals. The character of the correlation is determined by conjugation effects and polarity factors. If the reactivity of organic compound is determined by conjugation factor, i.e. by relative stability of the radical arising from the splitting of C-H bond, the more the reaction is accelerated by pressure the more reactive the hydrocarbon in respect to the radical is. Quantitatively the correlation may by expressed as the linear dependence of the log of the rate constant ratio of j-th reaction (k_j) to the rate constant of the standard reaction (k_i, toluene) on the difference in the respective activation volumes

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$(\varDelta V_f^{\neq} - \varDelta V_r^{\neq})$. Experimental data within the range of experimental errors fit the equation $\varDelta V_f^{\neq} - \varDelta V_r^{\neq} = -3.3 \log(k_f/k_r)$. The most considerable difference in the rate constants of the reaction is *ca.* 4 orders (Br, heptane, cumene) and it corresponds to the difference in the activation volumes about $12 \, cm^3/mol$.[46]

The obtained regularity is explained by the variety of $l^{\neq}$ distance in the transition state of the reactions of substitution involving hydrogen transfer.

$$-\overset{|}{\underset{|}{C}}H + \dot{X} \longrightarrow \left[-\overset{|}{C}\cdots\cdots H\cdots\cdots X\right] \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + HX$$
$$\underset{\longleftarrow \, l^* \, \longrightarrow}{|\qquad\qquad\qquad|}$$

In case of the given radical $\dot{X}$ one may say that the more stable the arising radical $-\overset{|}{\underset{|}{C}}\cdot$ is (the more easily the C-H bond is split) the less the distance $l^{\neq}$ is, *i. e.,* the more compact the transition state is the more the reaction is accelerated by pressure.

The rough evaluation of $l^{\neq}$ in various reactions was performed in the work[42] on base of the method proposed by Stearn and Eyring in the supposition that the degree of the lengthening of the formed and the split bonds in transition state remains the same and equals to *ca.* 10% in the case of the most rapid reaction. It proved that in the case of the most slow reactions which were studied the lengthening of the bond may rise up to 80%, more precisely the distance $l^{\neq}$ may undergo 80% increase. The possibility of these changes in l^* is supported by the estimation of positions of the transition state on base of the experimental data on activation energies and reaction heats.[51]

References. (47) and (48) report on the bromination of a number of toluenes. The velocity of the reaction is determined by polarity factors. The reaction is characterized by comparatively high value of ρ constant of Hammet's equation (-1.8). In this case the reverse correlation is observed; the slow reaction is more accelerated by pressure than the rapid one, however, and the linear dependence of log of the rate constants on activation volumes is still competent. No other possibility is found but to explain the dependence on base on changes in l^*. In this case the compactness of the transition state decreases with the decrease in electron accepting capacity of the substituent. Perhaps, when the shift of the electron pair of C-H bond towards the carbon atom occurs (slowing down of the reaction), Br atom should come into closer contact to include the electron into the orbit of the arising HBr bond. The presented quantitative dependence reveals itself more strictly in this case; 100-fold shift in the rate constant corresponds to the change in the activation volume *ca.* $10 \, cm^3/mol$.

2. Radical Reactions Induced by Deformation under Pressure

In 1937 Bridgman reported on the apparatus which permitted the simultaneous application of high pressure (up to 100 kbar) and shear shift to the thin layer (HP+SS).[52] With the use of HP+SS he tried more than 300 compounds including several tens of organic samples.[53] Not before twenty five years since Bridgman's work this trend in the field took its second

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birth (especially for organic compounds) mainly in works by Soviet investigators.

Various organic compounds proved to be capable to form compounds high molecular weight under the condition of HP+SS. This class includes quinones, nitriles, aromatic compounds, and some others. The first works which definitely showed the formation of high molecular compounds and polymerization phenomena by the deformation of organic compounds under pressure should be apparently dated 1968-69.[54,55] The review of pre-1972 works was done by Zharov.[56] The mechanism of these processes is unclear yet, though the data are available supporting in some cases the radical nature of polymerization under the condition of HP+SS. Thus, monomers which undergo ionic polymerization under usual condition are harder to be involved into the process at HP+SS than those which are polymerized by radical mechanism.[54] The studies on styrene—methyl-methacrylate showed that the distribution of the monomer links in the co-polymers at HP+SS is similar to that occurring in the co-polymers obtained by radical co-polymerization in the liquid phase.[57] However these data are indirect. A number of studies point out that the common methods proving the nature of polymerization may be hardly used at HP+SS. Thus, for instance, studies on polymer structure are often undertaken to obtain conclusions on the mechanism of polymerization. Meanwhile, the structure under the condition of HP+SS is apparently dependent upon the degree of destruction of the crystal lattice. The work[58] presents the results of the study on polymerization of 1,1,2-trichlorobutadiene-1,3 at HP+SS ($-75°C$). The structure of the obtained polymer was compared with those obtained by radical polymerization in the liquid phase ($100°C$) and in the solid phase ($-78°C$). The ratio of 1,4-to 3,4-links was compared. The ratio is 5-6 (solid phase), 1.95 (PH+SS), and 1 (liquid phase). The intermediate value of the ratio at HP+SS is supposed to be stipulated by considerable destruction of the crystal lattice of the monomer owing to plastic deformation. The supposition is made on base of the work[59] in which the solid phase polymerization of trichlorobutadiene at atmospheric pressure was studied.

The most close to the question which is considered in the actual review are the works[60-63] in which the polymerization of stable iminoxyl radicals, containing the groupings $C=C$,[60,63] $C\equiv N$,[61] and cyclopropane ring[62] was studied at HP+SS. According to the data,[60] the

iminoxyl radical $CH_2=CH-\overset{\overset{O}{\|}}{C}-NHR\cdot$ where R$\cdot$ is the group $-CH\overset{CH_2\text{——}C(CH_3)_2}{\underset{CH_2\text{——}C(CH_3)_2}{>}}N-O\cdot$, at

room temperature, shift angle $50°$, and 120 kbar yields insoluble polymer with the average polymerization degree $ca.$ 7. A molecule of the polymer contains in average one free radical site. The obtained data permit the scheme of the process which should occur in the liquid phase process at enough high temperature. The stable radical binds to the unsaturated bond of another radical and the new radical is involved into recombination with iminoxyl radical. So propagation of the chain goes this staged way. Polymerization of other stable radicals yields mainly in insoluble products which is apparently stipulated by the relative cross-linking of polymer molecules under the condition of HP+SS.

Studies on the polymerization of the ester of o-vinylbenzoic acid ($CH_2=CH-C_6H_4COOR$)

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showed the insoluble polymer to contain about 20% (of starting amount) of stable paramag-
netic sites while practically no double bonds occur.   One of the reasonable explanations of
this fact is the reaction of splitting of hydrogen atom off the polymer molecules by stable
polymer radical with the following formation of N-OH bond.   The groupings of this type are
known to react with air oxygen with the regeneration of the stable radical site.[64]   It is also
possible that sometimes HP+SS may provide conditions under which unsaturated groups
are more reactive than stable radicals.   The similar phenomena are also observed in case
of the stable radical containing $C \equiv N$ bonds.[61]   It should be added that the considered
polymerization of the ester of o-vinylbenzoic acid (contrary to p-isomer) is followed by
reactions leading to the destruction of benzene rings.   Ref. (65) reports on the formation of
oligomeric polyamides from unsaturated amide containing the iminoxyl radical site under the
condition of HP+SS, free radical site being not involved in the reaction.   Perhaps, this process
does not proceed via radical mechanism.

Studies on chemical transformations at HP+SS showed that in most cases simple compression
of solid samples up to 100 kbar did not lead to reaction.   The transformations follow the
applied shear shift and stop at the moment the deformation is stopped.   These and other
results provide the ground for the application of the methods of formal kinetics to the
description of the chemical processes at HP+SS.   Time in the differential equations is substi-
tuted by deformation.[66]   It should be pointed out that no correlation between velocity of the
processes at HP+SS upon the velocity of shear shift was observed.[61,67]   Thus, for instance,
the increase in rotation of the anvil at 70 kbar from 5.5 to 60 grad/min did not affect the
rate of nitrile polymerization.[61] while 50 grad turn at 70 kbar provide polymer in 33%
yield.   The velocity of deformation may be increased further, so it seems possible to perform
processes within tens of seconds and even seconds.

A question arises about the nature of such high reactivity of organic compounds at HP+SS.

Deformation of solid samples involves mechanical work which is mainly transformed into
heat, so considerable increase of temperature of the sample could be expected.   However,
direct measurements and calculations show that the increase in temperature can not exceed
15°.[68,69]

The hypothesis of the local heating[70] was also shown unapplicable to the explanation of
high velocities of the reactions.

There exists a natural supposition that the application of the shift removes diffusion
limitations for the reaction in the solid phase (thus, for instance, Ref. (71)).   According to this
supposition the considerable velocities of transformations at HP+SS may be explained with the
aid of the effect of high pressure, i.e. on base of well developed concepts on activation volumes.
However, even from this point of view, though diffusion limitation are reduced, most of
the actual experimental data can be scarcely understood and it may be clearly shown on
two examples.   The first is benzene polymerization including the opening of the aromatic ring
followed by the formation of polymer with well developed linear system of conjugated bonds.[72]

The reaction was not performed under any other conditions up to the date. The second is dimerization of cyclopentadiene by Diels-Alder's reaction.[73] The reaction easily proceeds under usual conditions, both activation energy and activation volume are available. Recent data permit the estimation of the rate of dimerization of cyclopentadiene in hypothetical liquid phase at temperature ($-120°C$), pressure (40 kbar), and within the period (1-2 minutes) usual for the experiments on solid cyclopentadiene under deformation. The dimerization rate in the liquid phase proves to be 9-10 orders lower than that observed under the condition of HP + SS.

It is pointed out in Ref. (73) that the nature of extremely high reactivity of organic compounds by deformation under compression is not clear yet. Nevertheless, the supposition is made that the applied shear shift causes the deformation of the valence bonds in molecules as well as the excitation of vibrational levels due to energy dispersion by plastic deformation of the sample. Perhaps, these phenomena stipulate the specificity of the reaction at HP+SS. Moreover, the deformation of the samples by compression leads to the destruction of crystal lattice and to relative shift of layers of the sample which provides mass transfer and apparently a certain orientation of molecules.

The data available nowadays show definitely that studies on chemical transformations under deformation in compressed solid materials present a new trend which is quite important in both theoretical and practical aspects.

Finally, the author wants to pay his pleasant debt by expressing his sincere gratitude to his collaborators G. A. Stashina and Z. G. Makarova for their help in preparing the manuscript and in carrying out some calculations.

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