ON THE APPLICATION OF HIGH PRESSURE TO THE STUDY OF COLLECTIVE INTERACTION IN POLYMERIZATION PROCESSES

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ON THE APPLICATION OF HIGH PRESSURE TO THE STUDY OF COLLECTIVE INTERACTION IN POLYMERIZATION PROCESSES

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At present it is generally recognized that the application of high pressure is very useful for investigating the transition state in chemical reactions; in particular, data on the influence of pressure on the rate of reactions in the liquid phase make it possible in a number of cases to arrive at definite conclusions about the structure of the transition state (see, for example, (^{1,2})), and also about the participation of the solvent in it ($^{3-6}$). The essence of the method consists in calculating, from the above-mentioned kinetic data, the magnitude of the volume change upon formation of the transition state and in comparing this magnitude with that expected on the basis of one or another model of the transition state. Thus it becomes possible to find the volume of the transition state itself. It is easy to see that this characteristic is very important in the study of collective interactions. Here one may be dealing with any processes associated with the necessity of overcoming a certain energy barrier and, in particular, with collective chemical interactions.

Let us write the equation expressing the dependence of the rate constant of a process k on pressure (^{7}):

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

Here $\Delta v^{\neq}$ is the change in volume upon formation of the transition state from the initial substances. If n particles participate in the transition state, then the quantity $\Delta v^{\neq}$ will, roughly speaking, be $(n-1)$ times larger than in the interaction of two particles.

As an illustration of the application of the method under consideration, let us cite the interesting data of Wentorf on the polymorphic transformation of diamond into graphite, reported at the XVII International Congress of Pure and Applied Chemistry in August 1959 (see also (^{8})). Wentorf found that the process of graphitization of diamond at temperatures of 1700–2200° is very strongly inhibited as pressure is increased. The value of $\Delta v^{\neq}$ found by him from kinetic data is about 168 cm^3 per 1 gram-atom, i.e., 50 times greater than the volume per 1 gram-atom in the crystal. From this the author drew the natural conclusion that the polymorphic transition he studied proceeds as a collective act involving a considerable number of atoms.

The above-considered polymorphic transformation of diamond into graphite is characterized by an increase in volume upon formation of the transition state. The opposite effect in sign is observed in polymerization reactions (see ([9])). Especially large compression upon formation of the transition state should occur in such polymerization reactions (at low temperatures or high pressures) in which one may assume the presence of collective interaction of the reacting particles ([10,11]). Such reactions should therefore undergo a very considerable acceleration with increas-

pressure. This may be illustrated by the following arbitrarily chosen example. Let the decrease in volume upon formation of the transition state with the participation of two monomer molecules (or of a radical with a molecule) be 10 cm^3 per mole, and let the number of particles participating in the transition state, n, be equal to ten. Then an increase in pressure by 1000 atm will lead, in accordance with equation (1), to an increase in the reaction-rate constant by a factor of 43.

It follows from the foregoing that investigation of the influence of pressure on the rate of polymerization in the liquid and solid phases can reveal cases of collective interaction of the reacting particles and make it possible to estimate the number of "participants" in this interaction.

Of great interest also is the study of the influence of temperature on the dependence of the rate constant on pressure. On the basis of a comparison of the Arrhenius equation with the equations of transition-state theory, the following equalities may be written*:

$$\left(\frac{\partial E}{\partial P}\right)_T = \left(\frac{\partial \Delta H^{\neq}}{\partial P}\right)_T ; \tag{2}$$

$$\left(\frac{\partial \ln A}{\partial P}\right)_T = \frac{1}{R}\left(\frac{\partial \Delta S^{\neq}}{\partial P}\right)_T . \tag{3}$$

Let us now make use of the known thermodynamic equations characterizing the dependence of heat content and entropy on pressure, and substitute them into (2) and (3):

$$\left(\frac{\partial E}{\partial P}\right)_T = \Delta v^{\neq} - T\left(\frac{\partial \Delta v^{\neq}}{\partial T}\right)_P ; \tag{4}$$

$$\left(\frac{\partial \ln A}{\partial P}\right)_T = -\frac{1}{R}\left(\frac{\partial \Delta v^{\neq}}{\partial T}\right)_P . \qquad (5)$$

According to the already cited data of Uentorff, the activation energy of the process of graphitization of diamond increases with increasing pressure from 0 (vacuum) to 20,000 atm, respectively from 175 to 255 kcal/g-atom. Substituting these data into equation (4), we find that the right-hand side of this equation is approximately equal to 165 cm^3/g-atom. Comparing this figure with the value $\Delta v^{\neq}$, equal to about 168 cm^3/g-atom (see above), we may conclude that the change of $\Delta v^{\neq}$ with temperature is close to zero. This means that, in the process under consideration, a change in temperature within the limits studied (1700–2200°) does not appreciably affect the number of atoms participating in the collective act of polymorphic transformation. Clarification of this question for collective chemical interactions will promote insight into the physical nature and mechanism of these processes.

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* Under the assumption that the transmission coefficient is independent of pressure.

Note: Figure translations are in progress. See original paper for figures.

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