Reports of the Academy of Sciences of the USSR

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1960

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1960. Volume 134, No. 2

PHYSICAL CHEMISTRY

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THE MECHANISM OF GAS FORMATION DURING THE RADIOLYSIS OF ORGANIC SUBSTANCES AND ITS RELATION TO THEIR AGGREGATE STATE

(Presented by Academician P. A. Rehbinder on 9 V 1960)

In studying the process of gas formation during the radiation destruction of polymers (polymethyl methacrylate, polytetrafluoroethylene), caused by the action of electron radiation, as a function of temperature, we showed (1,2) that in the region of transition of the irradiated* polymer from the highly elastic to the viscous-flow state (at temperatures $t \geqslant T_\tau$) the rate of gas evolution, at constant dose, increases sharply and discontinuously. We interpreted the mechanism of this phenomenon on the assumption that high local supersaturations of gas solutions arising as a result of radiolysis are dissipated by gas diffusion in the highly elastic "solid" state more slowly than in the "liquid" viscous-flow state, as a consequence of which, in the latter case, the formation of nuclei of a new gas phase and their growth are greatly facilitated. As a result, more rapid liberation of radiolysis products in a less viscous medium from the reaction sphere shifts to the left the equilibrium of the quasi-reversible process: destruction $\rightleftarrows$ recombination of free radicals—and increases the rate of gas formation. However, it was possible to suppose another explanation of this effect, for example, by considering it as the result of a radiation-induced lowering of the temperature of thermal destruction of the polymer, which is not connected with any changes in its physical state or conditional viscosity at the transition point (3)**. On the other hand, the more intense gas formation at $t \geqslant T_\tau$ could have been caused by a change in the very mechanism of the polymer destruction process, proceeding under these conditions in a manner characteristic of thermal decomposition—through detachment of monomer units from the ends of chains, in contrast to the usual radiation destruction at lower temperatures, which occurs through random chain scission (3).

A more unambiguous solution of the question of the correctness of the interpretation of the effect proposed by us could be approached by detecting this effect also under conditions of sufficiently low temperatures, at which the possibility of thermolysis is altogether excluded, and on substances of nonpolymeric nature. Ordinary organic substances of low molecular weight evidently satisfied this requirement. Thus, the aim of the present investigation was not the quantitative study of the process of gas forma-

* The temperature at which a change in the kinetics of gas formation occurs corresponds to the transition temperature not of the initial, but of the irradiated sample, because radiolysis of polymers undergoing predominantly destruction is accompanied, as shown by thermomechanical curves, by a decrease in their molecular weight and, consequently, in the transition temperature (^{2}).

** Radiation activation of thermal-destruction processes has been established by a number of authors (^{4,5}); however, in these works the question is not the influence of radiation on gas formation, but the enhancement, under the combined action of radiation and heating, of the processes of formation of condensable (liquid and solid) radiolysis products (^{4}) and the decrease under the same conditions of the chain-scission energy of macromolecules (^{5}).

···of gas formation during radiolysis as a function of temperature, but in the discovery of: 1) differences in the intensity of this process when organic substances are irradiated with the same dose in the liquid and solid states, and 2) agreement in the position of the temperature point of change in the kinetics of gas formation and the melting temperature (t_{m}) of the given compound.

Irradiation was applied to: *n*-octane, *n*-decane, paraffin, nitrobenzene, and *p*-dichlorobenzene (in the form of specially purified preparations from Kahlbaum, except for paraffin) at various temperatures by a beam of fast electrons in an accelerator installation operating at a voltage of 680–750 kV and at a dose rate varying in the interval $E_0 = 0.6 \div 1.9 \cdot 10^{18}$ eV/cm$^3 \cdot$ s; with a constant irradiation duration equal to 1 hour, the dose varied within $E = 2.2 \div 6.8 \cdot 10^{21}$ eV/cm^3. Dosimetry was carried out by the ferrous sulfate method. The temperature interval investigated for each compound covered the region below and above t_{m}; moreover, by thermostating (in a Geppler thermostat), under conditions of slight heating of the samples caused by irradiation, the temperature was maintained with an accuracy of up to $\pm 4°$. Therefore, by setting the experimental temperature exactly corresponding to the melting temperature, it was possible, in two experiments during irradiation of a sample, to establish the smallest temperature difference, respectively in the liquid and solid states (above and below the melting temperature), at 8°. Irradiation was carried out in a glass cuvette through a membrane 0.06–0.07 mm thick; the temperature was measured by a thermocouple, the junction of which was introduced through a glass pocket of the cuvette into the bulk of the sample. The amount of gaseous radiolysis products was measured by volume after their release from the sample, which was in the liquid state.

Fig. 1. Curves of the dependence of gas formation on temperature

Figure 1: Fig. 1. Curves of the dependence of gas formation on temperature

Fig. 1. Curves of the dependence of gas formation on temperature (arrows indicate the position on the abscissa axis of the melting temperature for each substance):
1 –*n*-decane, $E_0 = 1.2 \cdot 10^{18}$ eV/cm$^3 \cdot$ s, $E = 4.3 \cdot 10^{21}$ eV/cm^3;
2 –*n*-octane, $E_0 = 0.6 \cdot 10^{18}$ eV/cm$^3 \cdot$ s, $E = 2.2 \cdot 10^{21}$ eV/cm^3;
3 –paraffin, $E_0 = 1.1 \cdot 10^{18}$ eV/cm$^3 \cdot$ s, $E = 4.0 \cdot 10^{21}$ eV/cm^3;
4 –nitrobenzene, $E_0 = 1.9 \cdot 10^{18}$ eV/cm$^3 \cdot$ s, $E = 6.8 \cdot 10^{21}$ eV/cm^3;
5 –*p*-dichlorobenzene, $E_0 = 1.5 \cdot 10^{18}$ eV/cm$^3 \cdot$ s, $E = 5.4 \cdot 10^{21}$ eV/cm^3.

The measurement results are presented in Fig. 1 as curves of the dependence of gas volume on temperature, $Q = f(t)$.

As can be seen, the influence of a change in temperature on the formation of gaseous radiolysis products of the substances studied, when they are irradiated both in the solid and in the liquid state, is manifested very weakly (in accordance with the low values of the activation energy of such reactions) and with a practically identical temperature coefficient; however, in the transition region, at the melting temperature (indicated in Fig. 1 for each substance by an arrow), the process of gas formation changes suddenly (stepwise).

At the same time, the coincidence of the "critical" point corresponding to the change in the kinetics of the process with the melting point of the given compound is manifested very clearly and independently of the nature of the substance over a wide temperature interval, down to very low temperatures (in these experiments, down to $t = -56.5^\circ = t_\text{m}$ of octane). It is interesting to note that, analogously to organic compounds, water behaves in this way when irradiated as ice and in the liquid state, exhibiting an equally sharp change in the kinetics of gas formation at 0°.

The results obtained show that this feature of the radiolysis process is nonspecific, has a general character, and is characteristic not only of polymers, but also of low-molecular organic and inorganic compounds···

phenomena. It is associated with the conditions of gas formation accompanying radiolysis, and cannot be explained by considerations of an increase in thermal decomposition under the influence of radiation or by thermal activation of radiolysis, since in both of these cases the course of the curves would be characterized by a monotonically increasing effect of rising temperature.

Obviously, the phenomena represented by the curves in Fig. 1 are based on the same mechanism as that indicated above for polymers. At the same time, for low-molecular-weight substances there is a strict coincidence of the point of sharp increase in the rate of gas formation with the melting temperature, in contrast to polymeric substances, for which such a correspondence is observed in a more or less broad temperature region of polymer softening, which moreover changes in the course of irradiation of the polymer (2). The broad generality of the effect we have found for substances of the most varied composition and molecular structure, whose radiation-chemical reaction mechanisms are undoubtedly very different, makes it poorly justified to invoke the "cage effect" (6) to explain it, all the more since what is involved are differences in the process of gas formation that pertain only to condensed systems. It is more probable to assume that the rate of these reactions, which in the stage of formation of free radicals (i.e., before the moment of formation of nuclei of a new gas phase) have a reversible character, is inhibited to different degrees in irradiated objects in the solid and liquid states in accordance with the magnitude of the diffusion coefficients.

There are very few data in the literature that would make it possible to compare the permeability of the same organic compounds in different aggregate states; however, it may be noted, for example, that according to (7), the temperature coefficient of gas permeability (H_2, N_2, CO_2) through gutta-percha in the region of its softening (42—50°) increases by more than one order of magnitude faster than at temperatures before and after this interval (while the polymer, even in the liquid state, retains a high viscosity). On the other hand, the diffusion and self-diffusion coefficients in metals in the solid and molten states are, in order of magnitude, respectively 10^{-9} and 10^{-5} cm^2/sec (8,9).

Therefore, differences in the diffusion permeability of the solid and liquid phases of organic substances with respect to the gases formed in them during radiolysis cause a sharp change in the rate of the gas-formation process in the region of transition through the phase-transformation point.

A study of the chemical composition of the gases formed during radiolysis of low-molecular-weight organic compounds and polymers under the indicated conditions may provide additional data for elucidating the mechanism of the effect under consideration.

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Received
4 V 1960

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