Reports of the Academy of Sciences of the USSR

1960

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1960. Volume 135, No. 2

PHYSICAL CHEMISTRY

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ON THE THEORY OF THERMALIZATION OF HOT HYDROGEN ATOMS AND THEIR INFLUENCE ON THE YIELD OF THE DIMER PRODUCT IN THE RADIOLYSIS OF ALKANES

(Presented by Academician A. V. Topchiev, June 3, 1960)

Under the action of ionizing radiation in organic compounds, excited molecules and excited ions are formed, some of which then decompose into smaller fragments—free radicals, ions, ion-radicals, etc. If the decomposition reaction of an excited molecule or excited ion occurs in the gas phase, then, as can readily be shown with the aid of the laws of conservation of energy and momentum, part of the energy released in this reaction is converted into kinetic energy of translational motion of the fragments. As a result, the fragments may become "hot," i.e., acquire kinetic energy substantially exceeding the average energy of thermal motion at the given temperature. If the excited molecule decomposes into fragments of different masses, the greatest kinetic energy will belong to the lightest fragments. Thus, for example, in the radiolysis of alkanes hot alkyl radicals will be formed only upon rupture of a C—C bond, whereas upon rupture of a C—H bond only hydrogen atoms can prove to be hot. In this article, for definiteness, we shall speak only of hot hydrogen atoms.

The passage of a hot hydrogen atom through a gaseous hydrocarbon is accompanied by elastic and inelastic collisions with gas molecules, in which part of the energy of the hot atom is lost. Ultimately the hot atom becomes thermal. In an inelastic collision with a molecule, the hot atom may excite this molecule or cause a chemical reaction. As a result, the presence of hot atoms changes the course of radiolysis and affects the yield of the final products.

Since the energy thresholds of chemical reactions are different, the rates of reactions caused by hot atoms are determined by their energy spectrum at each point of the medium at each instant of time. The spatial-energy distribution can be determined by solving the gas-kinetic Boltzmann equation; however, this

is very difficult. Therefore, for this purpose we use an approximate method—the so-called method of energy groups, often applied in the theory of slowing down and thermalization of neutrons ([1], [2]). This method consists in describing the passage of hot hydrogen atoms by a system of diffusion equations for different monoenergetic groups of atoms, the atoms being able to pass from a higher energy group to a lower one.

1. We shall first confine ourselves to a two-group approximation and consider a group of hot atoms and a group of thermal hydrogen atoms. We shall assume that, in an inelastic collision with a molecule, a hot hydrogen atom causes the appearance of a new radical. This, of course, does not exhaust all possible reactions of a hot hydrogen atom with a paraffin molecule, but the principal features of radiolysis in the presence of hot atoms can be more simply

it is precisely on such a model that everything can be traced. Let us note that, owing to the short lifetime of a hydrogen atom in the "hot" state, collisions of the hot hydrogen atom with radiolysis products, including hydrogen atoms and alkyl radicals, may be neglected. Therefore the equation for the group of hot atoms will contain only the density of hot atoms, and will then be linear. Indeed, there are considerably fewer radiolysis products than molecules of the initial substance, while the slowing down of hot atoms (transition into the thermal group) occurs in collisions with any molecules, and its rate is in fact determined, consequently, by the number of collisions with the initial molecules; in other words, before a hot atom collides, for example, with another hydrogen atom, it will have time to undergo a sufficient number of collisions with initial molecules to pass into the thermal group.

The application of the two-group method is equivalent in our case to the assumption that hot and thermal hydrogen atoms are particles of two different kinds, and that particles of one kind may be transformed into particles of the other kind. Therefore, in the case of nonoverlapping tracks, the system of equations for one track, describing diffusion, recombination, and the appearance of free radicals of different types, as well as the process of thermalization of hot hydrogen atoms, may be written as follows:

$$\frac{\partial n_i}{\partial t} = D_i \Delta n_i - \sum_{j=1}^{m} a_{ij} n_i n_j - a_{iH} n_i n_H + A_i n_h + S_i, \tag{1a}$$

$$\frac{\partial n_h}{\partial t} = D_h \Delta n_h - \Lambda n_h + S_h, \tag{1 }$$

$$\frac{\partial n_H}{\partial t} = D_H \Delta n_H - \sum_{i=1}^{m} a_{iH} n_i n_H - a_{HH} n_H^2 + (\Lambda + \Lambda_H) n_h + S_H, \tag{1 }$$

where D_i is the diffusion coefficient of radicals of the i-th type; a_{ij} is the recombination coefficient of radicals of the i-th and j-th types; S_i is the number of radicals of the i-th type created per unit time in a unit volume of the track by the ionizing particle; A_i is the macroscopic effective cross section for formation of a free radical of the i-th type by a hot hydrogen atom; Λ is the macroscopic effective cross section for collisions of a hot atom with gas molecules, accompanied by its transition into the thermal group; n_i is the density of radicals of the i-th type; all quantities referring to hot hydrogen atoms are denoted by the subscript h, and those referring to thermal atoms by the subscript H. The term $\Lambda_H n_h$ describes the appearance of thermal hydrogen atoms upon decomposition of molecules excited by hot atoms. Atomic hydrogen, owing to its high mobility, rapidly diffuses from the track into the surrounding medium, where the density of alkyl radicals is small. Therefore the terms $a_{iH} n_i n_H$ may be neglected. Then the system of equations (1a) and (1) becomes independent of equation (1), and we shall consider only these two equations.

Let us consider an example. Suppose that, at the instant of track formation t_0, hot atoms are formed at a point with radius vector $\mathbf{r}_0$, and inside a sphere of radius R centered at the same point there are free radicals of one type (we shall therefore omit the index i). Then $S = Q\delta(t - t_0)\eta(R - |\mathbf{r} - \mathbf{r}_0|)$; $S_h = q\delta(t - t_0)\delta(\mathbf{r} - \mathbf{r}_0)$; Q and q are constants; $\eta(x) = 1$ for $x > 0$, $\eta(x) = 0$ for $x < 0$. The spherical-track model under consideration imitates one "bead" of an electron track. Moreover, the qualitative conclusions should not depend on the shape of the track, and the calculation in the case of a spherical track is considerably simpler than, for example, for a cylindrical track. Solving the system of equations (1a) and (1) by the method of successive approximations ([3]), using formula (12) of work ([3]) for $w = \text{const}$, we find in

in the first approximation, that the yield of the dimeric product is given by the formula

$$\rho = \frac{aQ^2w}{(4\pi)^{9/2}D'^{1/2}Vt}\int_0^t dt_0\int_V dr_0\int_V dr''\int_V dr'\int_0^\infty dt''\times$$
$$\times\frac{\eta\left(R-|r'-r_0|\right)}{(t''-t_0)^3(t-t'')^{3/2}}\exp\left\{-\frac{(r''-r')^2}{2D(t''-t_0)}-\frac{(r-r'')^2}{4D(t-t'')}\right\}+$$
$$+\frac{2aQAqw}{(4\pi)^{9/2}D^3D_h^{1/2}Vt}\int_0^t dt_0\int_V dr_0\int_V dr''\int_V dr'\int_0^\infty dt''\int_0^\infty dt'\times$$
$$\times\frac{\exp\{-\Lambda(t'-t_0)\}\eta\left(R-|r'-r_0|\right)}{(t''-t_0)^{3/2}(t'-t_0)^{3/2}(t''-t')^{3/2}(t-t'')^{3/2}}\times$$
$$\times\exp\left\{-\frac{(r''-r')^2}{4D(t''-t_0)}-\frac{(r'-r_0)^2}{4D_h(t'-t_0)}-\frac{(r''-r')^2}{4D(t''-t')}-\frac{(r-r'')^2}{4D(t-t'')}\right\}+$$
$$+\frac{aA^2wq^2}{(4\pi)^{15/2}D'^2D_h^3Vt}\int_0^t dt_0\int_V dr_0\int_V dr''\int_V dr'\int_0^\infty dt''\int_0^\infty dt'\frac{\exp\{-2\Lambda(t'-t_0)\}}{(t'-t_0)^3(t''-t')^3(t-t'')^{3/2}}\times$$
$$\times\exp\left\{-\frac{(r'-r_0)^2}{2D_h(t'-t_0)}-\frac{(r''-r')^2}{2D(t''-t')}-\frac{(r-r'')^2}{4D(t-t'')}\right\}. \tag{2}$$

The first term of (2) gives the yield of the dimeric product in the absence of hot atoms; the second and third terms give the additional yield of the dimer due to the action of hot hydrogen atoms; $\Lambda = A + F$, where F is the macroscopic cross section for elastic scattering of hot hydrogen atoms on gas molecules. From (2) it is seen that the addition, for example, of helium atoms leads to a decrease in the effect of hot hydrogen atoms, since as Λ increases the last two integrals decrease, while the first integral does not depend on Λ.

A more detailed investigation of formula (2) in the general form is difficult. Calculations by formula (2) can be carried out by numerical methods if all the coefficients entering into it are known.

2. In the case when the dose rate of ionizing radiation is so large that the spurs completely overlap and reactions proceed not in them but throughout the entire irradiated volume, the group equations are greatly simplified, and the application of the multigroup method makes it possible to calculate easily the yields of various chemical reactions caused by hot atoms. Indeed, for a homogeneous distribution of hot atoms in the system, the diffusion terms vanish. If, moreover, the established stationary distribution of hot atoms is considered, then in the group equations all time derivatives also become zero.

Let us denote: n_i as the stationary density of hot atoms with energy E_i (belonging to the i-th group); N as the number of molecules of the initial substance per unit volume; S_i as the number of hot atoms of the i-th group created by the radiation per unit volume per unit time; σ_i as the effective cross section for elastic scattering of a hot atom of the i-th group on a molecule, leading to its

transition to the $(i+1)$-th group; σ_{ik} and σ_{ic} as the total effective cross sections of all inelastic collisions of a hot atom of the i-th group leading to transition to the k-th group $(k > i)$ or, respectively, to absorption. Then the system of group equations is written as follows:

$$N\left(\sigma_i + \sum_{k=i+1}^{n} \sigma_{ik} + \sigma_{ic}\right) n_i = N\left[\sigma_{i-1} n_{i-1} + \sum_{k=1}^{i-1} \sigma_{ik} n_k\right] + S_i \quad (1 \le i \le m-1); \tag{3a}$$

$$N\sigma_{mc} n_m + a_{HH} n_m^2 + \sum_i a_{H\mu} n_m n_{R,\mu} = N\left(\sigma_{m-1} n_{m-1} + \sum_{k=1}^{m-1} \sigma_{mk} n_k\right) + S_m \tag{3 }$$

($n_{R,\mu}$ is the density of free radicals of type μ). Equation (36) refers to thermal hydrogen atoms.

Having solved the algebraic system (3), one can easily write the expression determining $\rho^{(\alpha)}$—the number of elementary acts of various reactions occurring per unit volume per unit time. For reactions $H + M$, in which a hydrogen atom disappears, we find

$$\rho^{(\alpha)} = N \sum_{i=1}^{m} \sigma_{ic}^{(\alpha)} n_{i0}, \tag{4}$$

and for reactions accompanied by the transition of a hot atom from the i-th group to the k-th, we may write

$$\rho^{(\alpha)} = N \sum_{i=1}^{m-1} \sigma_{ik}^{(\alpha)} n_i. \tag{5}$$

If the reaction threshold $E^{(\alpha)}$ satisfies the inequalities $E_{i_0} < E^{(\alpha)} \le E_{i_0-1}$, then in (4) and (5) all $\sigma_{ik}^{(\alpha)}$ and $\sigma_{ic}^{(\alpha)}$ with $i > i_0 - 1$ become zero.

The method described can also be used to study the kinetics of processes occurring with the participation of hot molecules, radicals, or ions. It can be used in radiochemistry, photochemistry, and thermochemistry.

In conclusion, I express my sincere gratitude to L. S. Polak and N. Ya. Chernyak for discussing the results of the work.

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Received
3 VI 1960

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