Reports of the Academy of Sciences of the USSR

1960

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1960. Volume 135, No. 2

PHYSICAL CHEMISTRY

Yu. A. KOLBANOVSKII and L. S. POLAK

KINETIC EQUATIONS OF NONCHAIN MONOMOLECULAR RADIATION-CHEMICAL REACTIONS

(Presented by Academician A. V. Topchiev on 3 VI 1960)

In recent years numerous experimental works have been published on the study of radiation-chemical reactions proceeding by a nonchain mechanism. In individual works, kinetic equations are derived for specific reactions. However, for a number of practically important cases, such, for example, as inhibited radiolysis of hydrocarbons or radiolysis at large integral doses, not only general but also particular kinetic equations are lacking.

In the present communication, various nonchain monomolecular radiation-chemical processes are considered in which the substance X participates. It is assumed that the substance X has two types of excited state: $X^*_{(1)}$ and $X^*_{(2)}$, and an arbitrary number m of decay pathways.* All equations refer to the rate of consumption of the initial substance.

I. **Region of small integral doses.** By small doses here are meant such doses at which one may neglect the consumption of the initial substance and the inhibiting action of the final products.

In this region the following processes occur (we shall first consider one type of excitation):

1. $X \rightsquigarrow X^*$ excitation by radiation.
2. $X^* \rightarrow X\ (+h\nu)$ dissipation and luminescence.
3. $X^* \rightarrow$ products (m pathways of decay or isomerization).

Accordingly:

$$W_1 = K_1 I, \tag{1}$$

where I is the differential dose rate in eV/cm^3 · sec;

$$W_2 = K_2[X^*]; \tag{2}$$

$$W_3 = \sum_{i=3}^{m} K_i[X^*]. \tag{3}$$

For the stationary case

$$W_1 = W_2 + W_3. \tag{4}$$

Substituting (1)–(3) into (4), we find that

$$[X^*] = \frac{K_1 I}{\sum\limits_{i=2}^{m} K_i}. \tag{5}$$

Substituting $[X^*]$ in (3) by (5), we obtain

$$W_3 = -d[X]/dt = K_1 I \sum_{i=3}^{m} K_i \Big/ \sum_{i=2}^{m} K_i. \tag{6}$$

Since the occurrence of each of the types of excitation takes place independently, an expression analogous to (6) may also be written for the consumption of substance X through another type of excitation. Therefore, in the general case, the desired rate of consumption of substance X will be represented by the sum of two expressions of the form (6). Combining the constants, we find

$$W_3 = I\left(\frac{K_{(1)1}\overline{K}_{(1)3}}{K_{(1)2} + \overline{K}_{(1)3}} + \frac{K_{(2)1}\overline{K}_{(2)3}}{K_{(2)2} + \overline{K}_{(2)3}}\right). \tag{7}$$

Since $W_3 = G_{(-X)}I$, where $G_{(-X)}$ is the radiation-chemical yield of substance X in molecules per 1 eV of absorbed energy, then

$$G = \frac{K_{(1)1}}{K_{(1)2}/\overline{K}_{(1)3} + 1} + \frac{K_{(2)1}}{K_{(2)2}/\overline{K}_{(2)3} + 1}. \tag{8}$$

It follows from (8) that the value of the radiation-chemical yield depends on two parameters: K_1, which determines the yield of excited molecules per unit dose rate, and $K_2/\overline{K}_3$, which represents the ratio of the rate constant of dissipation

---

* If one follows the assumptions made in work (^{1}), then $X^*_{(1)}$ and $X^*_{(2)}$ may be interpreted as the triplet and singlet types of excitation.

and luminescence to the sum of the rate constants of the elementary act of decomposition. Obviously, in the case of molecules with a conjugated bond system and, especially, of luminophores, the ratio $K_2/\overline{K}_3$ will be relatively large and the value of G, correspondingly, smaller than for molecules not possessing such a bond system.

Let us note that if one or several decomposition paths are reversible, then in the right-hand sides of (6) and (7) there must also appear, with a minus sign, an expression corresponding to the sum of the rates of the reverse reactions.

II. **Kinetics of a radiation-chemical reaction with small additions of an inhibitor providing "sponge" -type protection.** By "small additions" here is meant such a concentration of inhibitor at which the change in the concentration of the initial substance X may be neglected, so that the absorbed energy may be attributed entirely to the principal substance.

In such a system, in addition to the processes considered above, it is also necessary to take into account the process of excitation transfer, which may be written in the form

$$4. \quad X^* + \mathrm{B} \rightarrow X + \mathrm{B}^*,$$

where B is an inhibitor molecule; the rate of such a process is

$$W_4 = K_4[X^*][\mathrm{B}]^{n/3}. \tag{9}$$

For a reaction in the gas phase $n = 3$ (in general, n is an integer, $n \leq 3$), and the notation (9) is usual for a bimolecular reaction. However, in condensed systems mechanisms of excitation transfer are known that are not associated with collision (see, for example, ([2])). Consideration of possible values of n in condensed systems is a separate question lying beyond the scope of our communication.

III. **Radiation-chemical reactions at medium integral doses with accumulation in the reaction products of excitation acceptors providing "sponge"-type protection.** In this case, such a region of integral doses is considered in which it is already impossible to neglect inhibition of the process by the final products, but it is still possible to neglect consumption of the initial substance X.

In our treatment we assume that excitation acceptors are formed in the decomposition of one of the types of excited molecules, for example $X^*_{(2)}$, and inhibit decomposition along the other path by removing excitation of the type $X^*_{(1)}$. Then

$$W_{(2)3} = \bar{K}_{(2)3}[X^*_{(2)}] = \frac{d[A]}{dt}, \tag{10}$$

where A is the excitation acceptor.

It is also necessary to take into account the process:

5. $X^*_{(1)} + A \to A^* + X$, whose rate is

$$W_5 = K_5[X^*_{(1)}][A]^{n/3}, \tag{11}$$

where n has the values indicated above. Taking process 5 into account,

$$W_3 = W_{(2)3} + (W_{(1)3} - W_5). \tag{12}$$

The stationarity condition for $[X^*_1]$ will be

$$W_{(1)1} = W_{(1)2} + W_{(1)3} + W_5, \tag{13}$$

whence

$$[X^*_{(1)}] = \frac{K_{(1)1}I}{K_{(1)2} + K_{(1)3} + K_5[A]^{n/3}}. \tag{14}$$

Substituting the corresponding values into (13) and combining the coefficients, we obtain

$$W_3 = I\left(\bar{K}_{(2)} + \frac{1}{\bar{K}_{(1)} + \bar{K}_A[A]^{n/3}}\right). \tag{15}$$

In this case, as follows from (15), the reaction rate decreases with time (with dose), since $[A]$ increases with increasing integral dose.

IV. **General equation.** In the general case one should take into account not only the accumulation of excitation acceptors among the reaction products, but also the consumption of the initial substance; then (15) must be rewritten in the form

$$W_3 = I[X]\left(\bar{K}_{(2)} + \frac{1}{\bar{K}_{(1)} + \bar{K}_A[A]^{n/3}}\right). \tag{16}$$

It follows from the general equation (16) that, in the region of large integral doses, the reaction rate decreases especially rapidly, since $[X]$ decreases simultaneously and the concentration of excitation acceptors increases.

V. **Kinetics of a radiation-chemical reaction inhibited by small additions of a substance that affords protection by the "sacrificial" mechanism.** In considering such a system we shall take into account a process analogous to 5:

6. $X^*_{(1)} + D \to X + D^*$.

If the probability of decomposition of D^* is equal to unity, then the final equation will have the form (15):

$$W_3 = I \left(\bar{K}_{(2)} + \frac{1}{\bar{K}_{(1)} + \bar{K}_D [D]^{n/3}} \right) \tag{17}$$

with the difference, however, that $[D]$ decreases with time. In the more general case, when the probability of decomposition of D^* is not equal to unity, the following occur:

7. $D^* \to D$, with $W_7 = K_7[D^*]$.
8. $D^* \to$ decomposition, with $W_8 = K_8[D^*]$.

Then the consumption of D depends, in addition to W_6, on the ratio $W_8/W_7 = K_8/K_7$. The ratio of these constants will enter into the new value of K_D, and the form of equation (17) will not change.

VI. Kinetics of a monomolecular radiation-chemical reaction of an additive substance X in a medium where energy transfer occurs from the medium M to the additive*

In the case where the direct action of radiation on the additive substance X cannot be neglected, in addition to 1-3 the following processes take place:

$$\begin{array}{rll} 9. & M \rightsquigarrow M^*, & W_9 = K_9 I, \\ 10. & M^* \to M, & W_{10} = K_{10}[M^*], \\ 11. & M^* + X \to M + X^*, & W_{11} = K_{11}[M^*][X]^{n/3}. \end{array}$$

In the case under consideration, two stationarity conditions may be written for M^* and X^*, respectively:

$$W_9 = W_{10} + W_{11}, \tag{18}$$

$$W_1 + W_{11} = W_2 + W_3. \tag{19}$$

From (18) and (19) one obtains

$$[M^*] = \frac{K_9 I}{K_{10} + K_{11}[X]^{n/3}}; \tag{20}$$

$$[X^*] = \frac{K_1 I[X]}{K_2 + K_3} + \frac{K_{11}}{K_2 + K_3}[M^*][X]^{n/3}. \tag{21}$$

Replacing $[M^*]$ in (21) by (20) and multiplying both sides of (21) by K_3, we obtain the desired expression

$$W_3 = K_3[X^*] = \frac{K_1 K_3 I[X]}{K_2 + K_3} + \frac{K_3 K_9 K_{11} I[X]^{n/3}}{(K_2 + K_3)\left(K_{10} + K_{11}[X]^{n/3}\right)}. \tag{22}$$

For $K_2 = 0$ and $n = 3$, formula (22) is identical to the formula derived by V. A. Krongauz and Kh. S. Bagdasar'yan for the case of radiolysis of benzoyl peroxide in benzene medium (^{3}). Unfortunately, the authors of (^{3}) did not specify the circumstances under which one may assume $K_2 \ll K_3$, nor the concentration range where $n = 3$ (in the liquid phase).

In conclusion, we note that the relations derived above encompass all the principal classes of monomolecular nonchain radiation-chemical reactions, which makes it possible to design experiments specifically directed toward the investigation of the kinetic parameters of radiation-chemical processes.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
3 VI 1960

REFERENCES CITED

1. M. Burton et al., *J. Chem. Phys.*, **26**, 1337 (1957).
2. S. C. Ganguly, N. K. Chaudhury, *Rev. Mod. Phys.*, **31**, 990 (1959).
3. V. A. Krongauz, Kh. S. Bagdasar' yan, in: *The Action of Radiations on Inorganic and Organic Systems*, Publishing House of the Academy of Sciences of the USSR, 1958.

---

* The consideration is carried out under the assumption of negligibly small decomposition of the medium molecules. In the general case, K_{10} will be the sum of the rate constants of two processes.

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