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Abstract

Full Text

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ON THE HETEROLYTIC FORMATION OF FREE RADICALS IN THE RADIOLYSIS OF SOLID ORGANIC SUBSTANCES

The use of the EPR (electron paramagnetic resonance) method and of low temperatures has in recent years made it possible to deepen substantially our ideas about the primary chemical acts occurring in organic substances under the action of ionizing radiation.

Analysis of a large body of data on the measurement of radiation yields (G_R and G_{H2}) and on the determination of the structure of the primary radicals during irradiation of saturated (RH) and aromatic (ArH) hydrocarbons of various structures has made it possible to formulate a single, logically closed scheme for the radiolysis of substances of this kind ([1], [2]). On the basis of this scheme it is possible to predict the radiation stability and the direction of primary processes in various RH and ArH. An important distinctive feature of this mechanism is the assumption of the primary homolytic rupture of one of the C—H bonds. This assumption makes it possible to reconcile the experimental results with the well-known Frank–Rabinowitch rule ([3]) concerning the very small probability of formation, in the course of the primary act, of two heavy radicals in immediate proximity to one another (the so-called "cage" effect).

Recently, indications have appeared in the literature that radicals $\dot{R}$ may also be formed in the primary act during the radiolysis of compounds of the type RX, where X is a halogen atom ([4], [5]) or a polar group. If the purely homolytic mechanism of the primary act is still assumed, then the formation of $\dot{R}$, accompanied in each case by the formation of the radical $\dot{X}$, proves to be in contradiction with the Frank–Rabinowitch rule mentioned above. Therefore, to explain the formation of radicals $\dot{R}$ in the radiolysis of compounds of the RX type, it is necessary to assume the existence of some new elementary act.

As such a process we propose to consider the reaction of heterolytic decomposition of the excited particle $(RX)^*$:

$$(RX)^* \rightarrow \dot{R} + X^- + (+)_{loc}, \tag{1}$$

or, in the case of an electropositive X:

$$(\mathrm{RX})^* \rightarrow \dot{\mathrm{R}} + \mathrm{X}^+ + (e)_{\mathrm{loc}}. \qquad (2)$$

These processes explain the appearance of radicals $\dot{\mathrm{R}}$ without violation of the cage rule, which permits the hope of relating the radiation stability of substances of the type under consideration to the ease of localization of positive (in the case of (1)) and negative (2) charge in the lattice of the substance RX.

Another variant of the occurrence of a process of type (1) may be localization of the electrons formed when an ionizing particle passes through the medium:

$$(\mathrm{RX})_n \rightsquigarrow (\mathrm{RX})_n^+ + e,$$

on a neutral molecule RX:

$$e + \mathrm{RX} \rightarrow \dot{\mathrm{R}} + \mathrm{X}^-. \qquad (1')$$

Such a notation naturally implies that somewhere in the system there remains a localized positive charge $(\mathrm{RX})_n^+$, in full agreement with (1).

Processes of type $(1')$ have repeatedly been invoked to explain mass-spectrometric results [6] and to explain the formation of hydrogen atoms during photoionization of various additives (Fe^{2+}, J^-, C_6H_6) in aqueous systems [7, 8]. In the latter case, ionization of the particle M leads to formation of a hydrogen atom according to the equation:

$$\mathrm{M} + \mathrm{H_2O} + h\nu \rightarrow \mathrm{M}^+ + \mathrm{OH}^- + \dot{\mathrm{H}}. \qquad (*)$$

In 1963, in the course of proving that chemical reactions of the solvated electron occur in the radiolysis of alcoholic media, Hamill, Guarino, et al. [9] showed that, upon irradiation of systems containing large amounts of $PhCH_2Cl$ and $PhCH_2OCOCH_3$, radicals $Ph\dot{C}H_2$ and, respectively, ions Cl^- and CH_3COO^- are formed.

On the basis of all that has been said, one may suppose that the radiolysis of compounds of the type RCH_2X (for electronegative X) can proceed both by the usual homolytic mechanism

$$(\mathrm{RCH_2X})_n \rightsquigarrow (\mathrm{RCH_2X})_n^+ + \mathrm{e}, \qquad (0)$$

$$(\mathrm{RCH_2X})_n^+ + \mathrm{e} \rightarrow (\mathrm{RCH_2X})_n^* \begin{cases} \rightarrow \mathrm{R\dot{C}HX} + \dot{\mathrm{H}}, \\ \rightarrow \mathrm{RCH_2X} + \mathrm{q}, \end{cases} \qquad (a)$$

and by one of two possible heterolytic mechanisms: of type (1)

$$(\mathrm{RCH_2X})_n^* \rightarrow (\mathrm{RCH_2X})_{n-1}^+ + \mathrm{X^-} + \mathrm{R\dot{C}H_2}. \qquad (\ )$$

or of type $(1')$

$$(\mathrm{RCH_2X})_n^+ + \mathrm{e} \rightarrow (\mathrm{RCH_2X})_{n-1}^+ + \mathrm{X^-} + \mathrm{R\dot{C}H_2}. \qquad (\ ')$$

For a quantitative kinetic analysis of the proposed schemes there is still, unfortunately, an insufficient amount of reliable data. Nevertheless, there are a number of observations that may be regarded as positive confirmation of the existence of the heterolytic mechanism.

Thus, in [10] it was shown that, under γ-irradiation of a number of normal alkyl iodides at 77°K, the structure of the primary radicals depends very strongly on whether the iodide is amorphous or polycrystalline. In amorphous samples the EPR spectrum consisted of 5-6 lines with a total spectral extent (at $\lambda = 3$ cm) of about $\Delta H_n \simeq 150$-160 G, which corresponds to the well-known spectra of normal alkyl radicals. In the case of polycrystalline samples the spectrum consisted of a considerably larger number of lines (up to 30) with $\Delta H_n \simeq 1500$ G. The only possibility for explaining this spectrum, which cannot be due to any alkyl radical, is the assumption of formation of a radical of the type $\mathrm{R\dot{C}HJ}$. In this radical the hyperfine splitting is due not only to $\dot{\mathrm{C}} - \mathrm{H}$ and $\dot{\mathrm{C}} - \mathrm{C} - \mathrm{H}$ interactions (with $\Delta H_n \leqslant 160$ G), but also to the iodine atom. The large magnetic moment ($2.8\,\mu_{\mathrm{nucl}}$) and $i = 5/2$ also make this assumption very probable. (For its definitive proof, of course, it is necessary to study the EPR spectrum of radicals of the type (RCHJ), obtained by some other route.)

If one proceeds from this hypothesis, then the result of [10] is explained by the fact that in an amorphous medium mechanism ( ) predominates, evidently because of the larger number of possibilities for localization of the positive charge, while in a polycrystalline medium mechanism (a) predominates.

Here it should be pointed out that recently an analogous change in the direction of the primary decomposition act was found in the photolysis of alcohols. In carrying out sensitized photodecomposition of $\mathrm{CH_3OH}$ at 77°K in acidic and basic media, it was found that in acidic media the primary act is associated with photo-transfer of an electron by a mechanism close to (*)

$$\mathrm{A^-\ (or\ B) + CH_3OH} + h\nu \rightarrow \mathrm{A\ (or\ B^+) + \dot{C}H_3 + OH^-},$$

where $\mathrm{A^-}$ is the anion of oxalic acid, and B is a benzene molecule.

In basic media, a mechanism involving the formation of additional OH^- ions is highly unlikely, and the reaction proceeds according to the usual scheme with photosensitization, entirely analogous to the homolytic scheme in radiolysis:

$$\mathrm{B^* + CH_3OH \rightarrow B + \dot{C}H_2OH + H}.$$

From all that has been said it follows that the nature of the primary act in the radiolysis of organic substances with a polar substituent depends extremely strongly on how effectively the given lattice can localize a charge of one sign or the other. By controlling this effectiveness through a change in the state of aggregation, the pH of the medium, or some other factor, it is possible to alter in a prescribed direction the chemistry and the rate of the primary act of radiolysis.*

Another very important consequence of the proposed general approach to the mechanism of radiolysis is a new way of analyzing the mechanism of accumulation of primary radiolysis products in both polar and nonpolar media. Indeed, although in the initial stages of radiolysis of compounds of the RH and ArH types the homolytic mechanism predominates, as free radicals accumulate in the system, whose electron affinity is sufficiently high, they can substantially change the course of radiolysis. In the case of $\dot{R}H$, when the initial molecules possess only a negligible affinity for charge, the influence of radicals may already be manifested at fairly small $[R]$. Conversely, in the case of aromatic molecules, disruption of the primary mechanism may appear only at considerably higher radical concentrations. This conclusion is in good agreement with the results of the recently completed work of V. I. Trofimov, I. I. Cheidze, and N. Ya. Buben ([11]), who found that although the initial radiation yield of free radicals (G_R) in the radiolysis of ArH is 20–40 times smaller than in the radiolysis of RH, the linear character of the radical-accumulation curve in ArH is preserved up to concentrations of $3\text{–}5 \cdot 10^{20}$ cm^{-3}, whereas in the case of RH the maximum values at the highest doses do not exceed $1\text{–}1.5 \cdot 10^{20}$ 1/cm^3. It should be noted that the conclusion concerning the possibility of charge localization on free radicals was formulated in ([12]) and demonstrated in a special study of the thermo- and photoluminescence of irradiated hydrocarbons another 1–1.5 years ago ([13]). There is every reason to believe that consideration of all these data from a unified point of view will make it possible to approach the analysis of the mechanism of accumulation of radiation defects during irradiation on the basis of the concept of the probability of localization of free charge in the lattice of the substance under study.

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* It should be noted that, according to the proposed hypothesis, during irradiation paramagnetic particles of the type $(RX)_n^+$ should be formed, which in principle should give an EPR signal. Such signals have not yet been observed by anyone. In a number of cases, however, coloration of irradiated samples is observed (see, for example, the amorphous samples in ([10])), which may be associated with the formation of localized charges.

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