PHYSICS

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1961

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Abstract

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ON THE MECHANISM OF INHIBITION OF RADIOLYSIS

(Presented by Academician V. N. Kondrat' ev, March 29, 1961)

In the present work the effects of inhibition of the radiolysis of organic systems by small additions of impurities are considered. This effect is interpreted here as a consequence of direct transfer of excitation to the impurity molecule*. According to an analysis of the work (^{2}), the inhibition of radiolysis in a liquid at very small additive concentrations (10^{-3}—10^{-4} mol/l) is in a number of cases proportional to $C_i^{2/3}$, where C_i is the inhibitor concentration. It follows from this that the rate of inhibition decreases no faster than $1/R^2$, where R is the mean distance to inhibitor molecules.

Let us first examine the following model problem. There is a molecule II excited by radiation (an ion, radical, etc.) (see Fig. 1). At a distance $R = |R|$ from it there is an inhibitor molecule I. Let us take a coordinate system with its origin near I. We shall assume that

$$r_I \ll r_{II} \simeq R, \tag{1}$$

where r_I and r_{II} are the current radius vectors of I and II. In accordance with the features of the particular radiolysis problem under consideration, we shall suppose that II is in an excited electronic state with excitation energy ω, equal to several electron volts. At the same time the inhibitor molecule I has a practically continuous system of levels in the region of excitation energy ω, with density $\rho(\omega) = dN(\omega)/d\omega$. The further discussion will be carried out in the system of units $\hbar = c = 1$, in which ωR may be either greater or less than unity. At the same time

$$\omega r \ll 1, \tag{2}$$

where r is the extent of the excitation regions of I or II.

Fig. 1. I —inhibitor, II —excited system

The matrix element of the effective perturbation energy, corresponding to the transition of II to the ground level and the excitation of I without emission of photons, will be taken in the form

$$U_{i\to f} = \int (j_{\alpha II}(r_{II}))_{fi} \frac{e^{i\omega(|r_I - r_{II}|)}}{|r_I - r_{II}|} (j_{\alpha I}(r_I))_{fi} (dr_I)(dr_{II}), \tag{3}$$

where the integration is over all space; $(j_{\alpha i})_{fi}$ $(i = I, II)$ are the matrix elements of the components of the current vector corresponding to the transitions under consideration and different from zero in the regions I and II, respectively. A formula of the form (3) is given, for example, in ([3]), p. 296, in Heaviside units. In (3) summation over the four components of the current vector is implied. However, since in the problem under consideration $j_i \sim 10^{-2} j_0$ $(i = 1, 2, 3)$, and since below we restrict ourselves to the dipole approximation, one may retain only the components j_0, i.e. the density of dis–

* A qualitative suggestion of such a path of inhibition was made earlier (see, for example, ([1])).

of charge redistribution. Bearing in mind the spatial separation of I and II, we expand the factor

$$\frac{e^{i\omega(|\mathbf{r}_I - \mathbf{r}_{II}|)}}{|\mathbf{r}_I - \mathbf{r}_{II}|}$$

as follows (see (3), p. 317):

$$\frac{e^{i\omega(|\mathbf{r}_I - \mathbf{r}_{II}|)}}{|\mathbf{r}_I - \mathbf{r}_{II}|} = \frac{i\omega}{4\pi} \sum_{lm} \varphi^*_{lm}(\omega r_I) \Phi_{lm}(\omega r_{II}), \tag{4}$$

where

$$\varphi_{lm}(\omega r_I) = (2\pi)^{3/2} i^l \frac{J_{l+1/2}(\omega r_I)}{\sqrt{\omega r_I}} Y_{lm}\left(\frac{\mathbf{r}_I}{r_I}\right),$$

$$\Phi_{lm}(\omega r_2) = (2\pi)^{3/2} i^l \frac{H^{(1)}_{l+1/2}(\omega r_2)}{\sqrt{\omega r_2}} Y_{lm}\left(\frac{\mathbf{r}_2}{r_2}\right).$$

Here J is the Bessel function, $H^{(1)}_{l+1/2}$ is the Hankel function of the first kind; Y_{lm} are spherical functions; m runs through values from $-l$ to l, and $r_I = |\mathbf{r}_i|$. By virtue of (1),

$$\varphi_{lm}(\omega r_1) \cong 4\pi \frac{(i\omega r_i)^l}{(2l+1)!!} Y_{lm}\left(\frac{\mathbf{r}_1}{r_1}\right). \tag{5}$$

Integral (3) will now be decomposed into a sum of products of integrals over regions I and II, with each subsequent term of the sum in l, according to (5), differing from the preceding one by an additional factor $\sim \omega r$. In consequence of (2), we shall retain only the first nonvanishing term of this sum; for it we take the term corresponding to an electric dipole transition $l = 1$ in the inhibitor molecule. As a result, taking into account (5) and the approximations mentioned above, we obtain

$$U_{i\to f} = \frac{\omega^2}{3} \sum_{m=-1}^{1} \int r_I (j_{0I}(r_I))_{fi} Y_{1m}\left(\frac{\mathbf{r}_I}{r_I}\right)(d\mathbf{r}_I)\times$$

$$\times \int \frac{i(2\pi)^{3/2} H^{(1)}_{3/2}(\omega r_{II})}{\sqrt{\omega r_{II}}} Y_{1m}\left(\frac{\mathbf{r}_{II}}{r_{II}}\right)(j_{0II}(r_{II}))_{fi}(d\mathbf{r}_{II}) = \frac{\omega^2}{3} \sum_{m=-1}^{1} J^{(1)}_m J^{(2)}_m. \quad (6)$$

Let us consider separately the integrals $J^{(1)}_m$ and $J^{(2)}_m$ entering into (6). The first of them is proportional to the off-diagonal matrix element of the operators of the components of the electric dipole moment D_{im},

$$J^{(1)}_m = \int r_I (j_{0I}(r_I))_{fi} Y_{1m}\left(\frac{\mathbf{r}_I}{r_I}\right)(d\mathbf{r}_I) = \sqrt{\frac{3}{4\pi}}(D_{Im})_{fi}. \quad (7)$$

Under the integral (7), let us carry out the transformation corresponding to passage to a coordinate system with origin near II (see Fig. 1):

$$\mathbf{r}'_{II} = \mathbf{r}_{II} - \mathbf{R}, \quad (8)$$

and direct one of the axes (the third) along $\mathbf{R}$. Then, substituting the explicit expression for the Hankel function appearing here, we obtain

$$J^{(2)}_m = -\frac{4\pi i}{\omega} \int \frac{1}{|\mathbf{r}'_{II} + \mathbf{R}|} e^{i\omega|\mathbf{r}'_{II}+\mathbf{R}|}\left[1 - \frac{1}{2i\omega|\mathbf{r}'_{II} + \mathbf{R}|}\right]\times$$

$$\times(j_{0II}(\mathbf{r}'_{II} + \mathbf{R}))_{fi} Y_{1m}\left(\frac{\mathbf{r}'_{II} + \mathbf{R}}{|\mathbf{r}'_{II} + \mathbf{R}|}\right)(d\mathbf{r}'_{II}). \quad (9)$$

Expanding (4) in the small parameter $\omega r'_{II} \cong r'_{II}/R$ and retaining only terms of zero and first order, we obtain

$$J^{(2)}_m = -\frac{4\pi i}{\omega R}\sqrt{\frac{3}{4\pi}} e^{i\omega R}\delta_{m0}\left\{\left[1 - \frac{1}{2i\omega R}\right]\int j_{0II}(\mathbf{r}'_{II} + \mathbf{R})_{fi}(d\mathbf{r}'_{II}) +\right.$$

$$\left. + \left[1 - \frac{3}{2i\omega R} + \frac{1}{(i\omega R)^2}\right]\int i\omega r'_{II}\cos\varphi\,(j_{0II}(\mathbf{r}'_{II} + \mathbf{R}))_{fi}(d\mathbf{r}'_{II})\right\}, \quad (10)$$

where φ is the angle between the directions $\mathbf{r}'_{II}$ and $\mathbf{R}$, and the Kronecker symbol δ_{m0}, arising from

$$Y_{1m}\left(\frac{\mathbf{r}'_{II}+\mathbf{R}}{|\mathbf{r}'_{II}+\mathbf{R}|}\right),$$

corresponds to retaining only the transverse-

···to R waves. The second integral in (10) is proportional to the off-diagonal matrix element of the component $m=0$ of the operator of the electric dipole moment of system II:

$$\int r'_{II}\cos\varphi\,(j_{0II}(r'_{II}+R))_{fi}\,dr'_{II} = (D_{IIm})_{fi}. \tag{11}$$

The first integral on the right-hand side of (10) for molecules and radicals is equal to zero for orthogonal wave functions i and f. In this case

$$J_m^{(2)} = \frac{(4\pi)^{1/2}\sqrt{3}}{R}\,e^{i\omega R}\delta_{m0}\left[1-\frac{2}{i\omega R}+\frac{3}{2(i\omega R)^2}\right](P_{I0})_{fi}. \tag{12}$$

Substituting (7) and (12) into (6), we obtain

$$U_{i\to f} = \frac{\omega^2 e^{i\omega R}}{R}\left[1-\frac{2}{i\omega R}+\frac{3}{2(i\omega R)^2}\right](D_{I0})_{fi}(D_{II0})_{fi}. \tag{13}$$

It follows from (13) that the probability of the process under consideration per unit time, summed over the final states of system I, is finally equal to

$$\begin{aligned} W_{if} &= \int 2\pi|U_{i\to f}|^2\delta(E_{fI}-\omega)\rho(E_{fI})\,dE_{fI} \\ &= 2\pi\frac{\omega^4}{R^2}\left(1+\frac{1}{(\omega R)^2}+\frac{9}{4(\omega R)^4}\right)\rho(\omega)(D_{I0})^2_{fi}(D_{II0})^2_{fi}, \end{aligned} \tag{14}$$

where the energy of the ground state of the inhibitor, E_{iI}, has been taken as zero. In passing to the specific problem of radiolysis under consideration, it may prove necessary to integrate (14) over the width of the excited level II, equal to Δ, and arising because of the possibility of chemical decomposition and luminescence. Since $\Delta \sim \hbar/\tau \ll 10^{-27}/10^{-13} \simeq 10^{-14}\,\mathrm{erg} \simeq 10^{-2}\,\mathrm{eV} \ll \omega$, the indicated integration reduces to interpreting the energy ω as the mean value over the width Δ and replacing $\rho(\omega)$ by $\displaystyle\int_{\omega-\Delta/2}^{\omega+\Delta/2}\rho(x)\,dx$. To estimate the magnitude of W_{if}, it is useful to express (14) in terms of the probabilities of dipole radiation of the excited molecules I and II, W_I and W_{II}. Starting from the known formula for polarized dipole radiation, we obtain, in the usual system of units,

$$W_{if} = \frac{9}{2^7\pi}\frac{\hbar^3c^2}{\omega^2R^2}\left[1+\frac{\hbar^2c^2}{(\omega R)^2}+\frac{9\hbar^4c^4}{4(\omega R)^4}\right]\rho(\omega)W_{IW_{II}}. \tag{15}$$

It is clear from (15) that the ratio W_{if}/W_I becomes sufficiently large if the density of levels $\rho(\omega)$ is large and W_{II} is small.

Let us pass from the model problem considered to the problem of determining the dependence of the rate of inhibition of radiolysis on the concentration of the inhibitor C_i. Since the excitation levels of the organic ions formed during radiolysis lie below the first electronic excited level of the corresponding molecules, the medium between the excited ion and the inhibitor is transparent. Strong absorption with appreciable inhibition must take place on the inhibitor molecules. In this connection, on passing to the medium we would have had to add to ω in formula (3) an imaginary term depending on the absorption probability. Instead, we shall take the final upper limit R_2 in determining the averaged probability of inhibition in the medium W:

$$W \simeq \int_{R_1}^{R_2} W_{if}(R)\,C_i\,(dR). \tag{16}$$

To estimate the dependence of W on C_i, the values of the mean distance to an inhibitor molecule R_1 and R_2 may be specified by the conditions

$$\frac{4}{3}\pi R_1^3 C_i \simeq 3; \qquad \frac{4}{3}\pi R_2^3 C_i = N(C_i); \qquad 3 < N(C_i) < 10. \tag{17}$$

Substituting (14) into (16), we obtain

$$W \simeq AC_i^{2/3}\left(1+\alpha_1 C_i^{2/3}/\omega^2+\alpha_2 C_i^{4/3}/\omega^4\right), \tag{18}$$

where A does not depend on C_i, and α_1, α_2 are numerical coefficients of order unity.

From consideration of formula (18) it follows directly that, in addition to the dependence of the inhibition rate on $C_i^{2/3}$ (for small values of C_i) established in (^{2}), one should expect that, as the concentration increases, the dependence of W on C_i will first pass through a transition region of relatively small extent, where all terms are significant, and then a region will set in where the determining term will be $C_i^{6/3}$. Comparison of these conclusions with experiment was intended to establish whether dependences on $C_i^{2/3}$ and $C_i^{6/3}$ do indeed occur. This should also make it possible to approach an estimate of the magnitude of the

Fig. 2

Figure 1: Fig. 2

transferred excitation energy ω, to compare this value with the electronic spectra of the corresponding inhibitors, and to determine the influence of the medium.

Fig. 2. Dependence of $1/(G{-}G_i) \sim W$ (where G_i is the radiation-chemical yield of the fully inhibited radiolysis of cyclohexane in the presence of J_2 according to ([4])): *a*—on $C_i^{2/3}$; *b*—on $C_i^{6/3}$.

In Fig. 2 are shown the results of processing the experiments ([4]), with only the fully inhibited process being considered, i.e., $G - G_i$ is taken. As is evident from the figure, formula (18) indeed correctly describes the course of inhibition of radiolysis over a wide range of variation of C_i. Processing of the results of experiments ([5–8]) led to analogous conclusions. In all cases, the values of ω found lie in those regions of the electronic spectra of the inhibitors where absorption is very significant (as a rule, values $\lg \varepsilon \simeq 4$) and, in character, close to continuous.

Thus, the general form of the dependence of the inhibition rate on C_i in the experiments considered confirms the formula derived, and it is possible to give a unified description over a broad region of C_i, including the so-called saturation region.* We note that the considerations developed can be applied to explain inhibition in a number of chemical reactions.

The authors express their gratitude to V. G. Levich, L. S. Polak, and the participants of the seminars conducted by them for discussions.

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Received
23 III 1961

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* It is interesting to note that the dependence of the rate of inhibition of radiolysis on $C_i^{6/3} = C_i^2$ at large C_i, cited here, was also established experimentally in an applied study (^{9}).

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

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