PHYSICAL CHEMISTRY

A. I. MIKHAILOV, I. S. GAPONOVA, Ya. S. LEBEDEV

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. I. MIKHAILOV, I. S. GAPONOVA, Ya. S. LEBEDEV

MIGRATION OF RADICAL STATES IN THE SOLID PHASE

(Presented by Academician V. V. Voevodskii, February 16, 1965)

1. At present there is great interest in the study of reactions of free radicals in the solid phase. It is obvious that, regardless of the specific reaction mechanism, in order for chemical interaction to occur the reacting centers must first come close together. Since the diffusional mobility of radicals at temperatures tens and hundreds of degrees below the melting point of the matrix often appears doubtful, many works (see ($^{1-3}$)) assume a migration mechanism for the displacement of valence according to the reaction

$$\mathrm{R^* + RH \xrightarrow{k_m} RH + R^*}. \qquad (1)$$

In specific cases it has been possible experimentally to observe the transfer of the radical state to neighboring molecules or to parts of molecules at low temperatures (see, for example, (^{4,5})); however, in the general case the fact of migration and its role in solid-phase reactions are unclear. It is all the more unclear what may limit the migration rate—the direct process of valence transfer or the corresponding internal motions of molecules, since reactions in the solid phase are often associated with the appearance of mobility of individual segments of molecules (^{6}) or of molecules as a whole (^{7,8}).

2. In view of the above, it is clear that "direct" observation of the displacement of radical states through a solid matrix would be of fundamental interest and would help to clarify the detailed mechanism of solid-phase reactions. In order to observe such displacement, we created large gradients of radical concentration in solids by generating radicals on the surface with the aid of a high-frequency discharge from a "Tesla" generator (^{9}). Samples in the form of finely dispersed powders were evacuated to $(2\text{–}5)\cdot 10^{-2}$ mm Hg and irradiated with the discharge, while the ampoule containing the sample was continuously washed by a stream of liquid nitrogen. Under these conditions, apparently, the temperature of the sample may be taken to be 77° K. Free radicals were then recorded on an EPR-2 spectrometer of the Institute of Chemical Physics. Particle size was usually determined by sieving through screens with mesh sizes from 50 to 100 μ and by subsequent determination of the sizes and shapes of the particles under a microscope. We usually used powders with $L = V/S = 1$–$10\,\mu$, i.e., with a specific surface from 0.1 to 1 m^2/g. The discharge intensity was monitored by the voltage at the input of the "Tesla" transformer and by the reproducibility of the accumulation curves.

Figures 1, a and 2 show typical accumulation curves of free radicals under the action of a high-frequency discharge obtained in this way. From Fig. 1, b it is seen that the accumulation kinetics is well described by the "diffusion" dependence $n = a+b\sqrt{t}$, with no deviation from a straight line in the coordinates $n, \sqrt{t}$ observed when the quantity changes by more than two orders of magnitude. The course of the accumulation curves does not depend on the ratio between the periods of irradiation and measurement. The EPR spectra of the recorded free radicals, in accordance with what was recently shown in (^{10}), practically always coincided with the spectra obtained upon irradiation of the same substances with γ-rays or fast electrons, although, as a rule, their hyperfine structure was somewhat less well resolved. From Fig. 3, a it is seen that

a similar pattern of accumulation is observed for the most diverse organic substances and polymers; moreover, after 1 hour of irradiation concentrations are reached that exceed by 1-2 orders of magnitude the limiting concentration corresponding to the maximum possible filling of the surface. On the other hand, the distribution of radicals over the volume is not uniform, because if at some point A of the accumulation curve (Fig. 2) a partial annealing of the radicals is carried out, then afterward accumulation proceeds with the same initial rate as under irradiation of a fresh sample, whereas with uniform accumulation over the volume and, consequently, uniform annealing of radicals, the rate of accumulation upon repeated irradiation would be considerably smaller (see Fig. 2, *b*—*g*). All data refer to one discharge intensity (voltage at the input of the "Tesla" generator 155 V). As the discharge intensity is increased, the rate of accumulation increases.

Fig. 1 Fig. 2

Fig. 1. Kinetics of accumulation of free radicals in thymine ($V/S = 1\,\mu$) under surface generation. *a*—in the coordinates n, t; *b*—in the coordinates $n, \sqrt{t}$.

Fig. 2. *a*—kinetics of radical accumulation in thymine; at point A partial annealing of radicals was performed; *b*—accumulation curve under repeated irradiation with a discharge; *v*—theoretical curve of "repeated" accumulation for a nonuniform distribution of radicals; *g*—the same for a uniform distribution.

3. On the basis of the experimental data obtained, the following model of "diffusional" accumulation of radicals may be proposed. In a low-pressure gas discharge, according to (^{9}), ionizing electrons have an energy of no more than 10-100 eV. Such electrons are capable of generating radicals only at a depth l_s of several monolayers of the crystal lattice (10-20 Å) (^{9}). In this layer the limiting concentration n_s is rapidly accumulated, and any further increase in the number of radicals can occur only at the expense of their migration into the depth of the sample. If k_m is the

Fig. 3

Figure 1: Fig. 3

frequency of "jumping" of a valence from one elementary cell to another, and λ is the lattice constant, then the mean thickness of the layer filled with radicals during time t will be

$$\delta \sim \lambda \sqrt{k_m t}, \tag{2}$$

and the total concentration of radicals

$$n \simeq n_s l_s \frac{S}{V} + n_s \delta \frac{S}{V}.$$

In order to take qualitative account of the kinetics of accumulation in the surface layer, we shall assume that the radicals disappear by a second-order reaction with rate constant k_2, and that diffusion "turns on" after a time

$\tau_s = 1/k_2 n_s$ after the onset of irradiation. Then we finally obtain:

$$\frac{n}{n_s} \simeq \frac{l_s}{L}\,\mathrm{th}(n_s k_2 t) + \mathrm{Re}\left\{\frac{\lambda}{L}\sqrt{k_m (t-\tau_s)}\right\}. \tag{3}$$

The accumulation curves calculated by formula (3) are shown in Fig. 3, *b*, from which it is seen that the proposed accumulation model is in good agreement with the experimental data (see Fig. 3, *a*).

Of course, one could try to interpret the observed regularities without invoking the hypothesis of migration of radical states. In particular, one may assume that radical generation occurs in a layer comparable with the thickness of the sample, owing to slowed electrons or secondary active centers (H atoms, excitations, etc.) migrating from the surface. In this case, however, the accumulation kinetics will never be purely diffusive and, as preliminary calculations have shown, it is very difficult to explain the fulfillment of dependences of type (3) over such a wide range of times and concentrations. Ideas about the diffusion of H atoms are not applicable here also because, in studying aromatic hydrocarbons, we observed the usual ratio of EPR spectra of "attachment and detachment"radicals, whereas in the diffusion of H one should expect preferential formation of "attachment radicals" (^{11}). In view of the above, the interpretation of the experimental data on

Fig. 3. *a* –linear anamorphoses of radical-accumulation curves under surface generation in various organic substances: 1 –paraffin, 2 –stearic acid, 3 –polyethylene, 4 –uracil, 5 –thymine, 6 –glycine, 7 –phenol, 8 –benzene. The

curves are numbered in accordance with Table 1. b –accumulation curves theoretically calculated by formula (3) for values of
$\lambda/L\sqrt{k_m\tau_s}$: I –0; II –0.5; III –1; IV –2.

on the basis of relations of the type (2) and (3) appears to us the most reasonable.

4. In this case, from the data of Fig. 3 one can estimate the rate constant of migration k_m.

As can be seen from the data of Table 1, radicals in stearic acid, paraffin, and polyethylene at 770°K possess a "mobility" 2-3 orders of magnitude greater than that of "small" radicals in benzene, glycine, etc. This argues in favor of the assumption of valence migration of type (1), since

Table 1

Estimate of the rate of migration of radical states in various organic substances upon irradiation by a discharge from the surface

No.	Substance	Experimental migration rate $\frac{\partial(nL)}{\partial(\sqrt{t})}\cdot 10^{-18}, \frac{\mu}{g\cdot min^{1/2}}$	Limiting concentration $n_s\cdot 10^{-20}$, g^{-1}*	Migration depth in 1 hour δ_1, μ	k_m, s^{-1}
1	Paraffin	10	2	0.39	170
2	Stearic acid	3.7	3	0.14	25
3	Polyethylene	12	3	0.36	160
4	Uracil	0.38	<1	>0.03	>10
5	Thymine	0.28	<1	>0.02	>0.5
6	Glycine	0.32	2	0.012	0.2
7	Phenol	0.2	0	0.15	25
8	Benzene	0.22	4	0.004	0.02

* From data on β-radiolysis ([12,13]).

with diffusion of the radical as a whole the effect should be the opposite. The independence of the accumulation kinetics from the duration of the dark periods, as well as the acceleration of accumulation with increasing discharge intensity, indicate that valence migration occurs only in the presence of radiation and, consequently, the values of k_m refer only to this discharge intensity. The phenomenon of acceleration of kinetic processes in a radiation field has been known for a comparatively long time ([14–16]); however, in the present case, apparently, valence migration takes place in that region of the solid into which high-energy particles do not penetrate. Therefore, in our view, it is more correct here to use the concept of a more "long-range" low-energy excitation of the solid matrix, which cannot break chemical bonds but is capable of activating internal motions and processes of valence transfer of type (1).

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
11 II 1965

CITED LITERATURE

1. A. T. Koritskii, Yu. N. Molin et al., *Vysokomolek. soed.*, **1**, 1182 (1959).
2. B. Loy, *J. Phys. Chem.*, **65**, 58 (1961).
3. S. E. Bresler, E. N. Kazbekov et al., *Fiz. tverd. tela*, **5**, 675 (1963).
4. V. K. Milinchuk, S. Ya. Pshezhetskii, *DAN*, **152**, 665 (1963).
5. P. Ausgough, H. Evans, *J. Phys. Chem.*, **68**, 3066 (1964).
6. Ya. S. Lebedev, Yu. D. Tsvetkov, V. V. Voevodskii, *Kinetika i kataliz*, **1**, 496 (1960).
7. R. Bensasson, M. Dupu et al., *Disc. Farad. Soc.*, **36**, 177 (1963).
8. N. Ya. Buben, A. I. Pritula, V. N. Shamshur, *Kinetika i kataliz*, **5**, 196 (1964).
9. C. Bamford, A. Jenkins, J. Ward, *Nature*, **186**, 712 (1960); *Polymer*, **2**, 277 (1961).
10. V. P. Golikov, A. G. Chetverikov, A. E. Kalmanson, *Free-Radical Processes in Biological Systems.* Symposium, abstracts of reports, Moscow, 1964, p. 16.
11. V. I. Trofimov, I. I. Chkheidze, N. Ya. Buben, *Zhurn. strukt. khim.*, **5**, 624 (1964).
12. V. V. Vasil' ev, V. L. Tal' roze, *Kinetika i kataliz*, **4**, 497 (1963).
13. V. I. Trofimov, I. I. Chkheidze, N. Ya. Buben, *Kinetika i kataliz*, **5**, 730 (1964).
14. M. A. Mokul' skii, *Vysokomolek. soed.*, **2**, 119 (1960).
15. N. S. Tikhomirova, Yu. M. Malinskii, V. L. Karpov, *Vysokomolek. soed.*,

2, 221 (1960).

16. E. L. Zhuzhgov, N. N. Bubnov, V. V. Voevodskii, *Kinetika i kataliz*, **6**, No. 1 (1965).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.