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Radical Pairs in the Study of Elementary Chemical Reactions in Solid Organic Substances

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Methods for the investigation of elementary chemical reactions and molecular motions on the basis of the EPR spectra of radical pairs are examined. The results of the study of the stereochemistry and kinetics of processes involving radical pairs are used to discuss the nature of the characteristic features of the elementary solid-phase reactions: the existence of a broad spectrum of the frequencies of the reactions and molecular motions, the reaction mechanisms at low temperatures, and the influence of intra- and inter-molecular motions on the rates of chemical reactions.
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I. INTRODUCTION

Studies on elementary chemical processes in solid organic substances, which were initiated to a large extent in the research of Academician V.V.Voevodskii[1], are developing vigorously at the present time. These studies are fundamentally closely related to fields of modern science such as the physical chemistry of polymers, molecular biology, and radiation chemistry. In contrast to elementary gas-phase reactions, where energy transfer, excitation, and excited state relaxation processes are most significant (and responsible for the rate of the chemical reaction), in the solid state an analogous role is apparently played by phenomena of a quite different type: translational and rotational motions, conformational rearrangements of molecules, etc.

In the study of reactive species in condensed media spectroscopic and microwave spectroscopic methods are of greatest importance. However, it is difficult to use even these methods to investigate elementary processes of the above type, because rotation and conformational transitions usually have only a weak influence and translational displacements have no influence at all on the spectra of individual species. The aim of the present review is to show that, in relation to radical reactions which play an important role in the chemistry of solid organic substances, considerable progress may be achieved by investigating radical pairs, i.e. radicals separated by a "molecular" distance (3–10 Å). Such radical pairs are, as it were, "entropically excited" intermediates in dissociation-recombination and disproportionation reactions. The high sensitivity of the EPR spectra of radical pairs to a relative displacement of the reaction centres has proved to be most significant, and makes it possible to obtain in many instances detailed information about the elementary processes in solids.

It has been shown a comparatively long time ago that, when stable radicals adjoin one another, the interaction between unpaired electrons greatly alters the spectrum. This permits the determination of the distance between the electrons[2]. There was a growth of interest in the "chemical" applications of this phenomenon after the discovery of the possibility of detecting metastable radical pairs, consisting of active radicals formed as a result of the decomposition of molecules in the solid phase[3]. Since 1966–1967, studies in this field have led to the detection and investigation of radical pairs in many chemical systems; these investigations have been surveyed in monographs[4,5] and reviews[6,7]. However, the above reviews were devoted mainly to problems of the formation of radical pairs and the analysis of their EPR spectra. As far as we are aware, the present review is the first attempt to survey new data on the kinetics of elementary physical and chemical processes obtained in the study of radical pairs. We hope that this survey will make it possible to formulate more clearly the possibilities arising as a result of the development of this field of research.

II. METHODS FOR THE INVESTIGATION OF RADICAL PAIRS

The theory of the EPR spectra of radical pairs has been described in detail in reviews[8,9] and monographs[10,11]. Here we shall consider the main theoretical conclusions directly applicable to the study of elementary reactions in the condensed phase.

1. EPR Spectra of Radical Pairs

A pair of radicals separated by distance $r \leqslant 10$ Å constitutes a system with two interacting electrons having an overall spin $S = 1$ and hence a multiplicity $2S + 1 = 3$. The dipole–dipole interaction between the electrons removes the degeneracy of the levels in the "zero field". The energy of the states and the transitions in the case of axial symmetry, where the energies of the T_1 and T_{-1} states in the zero field are the same, are illustrated in Fig. 1. When the magnetic field H_0 is scanned using a fixed frequency, it is possible to observe two allowed $\Delta M_S = 1$ transitions corresponding to the reversal of a single spin in the magnetic field. The splitting in this instance is

$$D = \frac{\xi g \beta}{r_{cp}^3}(3\cos^2\alpha - 1) \quad , \qquad (1)$$

where r_{av} is the length of the appropriately averaged vector connecting the unpaired electrons of the free radicals, α the angle between the interelectron vector $\vec{r}_{av}$ and the direction of the permanent magnetic field H_0, g the spectroscopic splitting factor, assumed to be isotropic, β the Bohr magneton, and ξ a numerical coefficient equal to 3/4 for resonance spins (having the same Larmor precession frequency) and 1/2 for non-resonance spins.

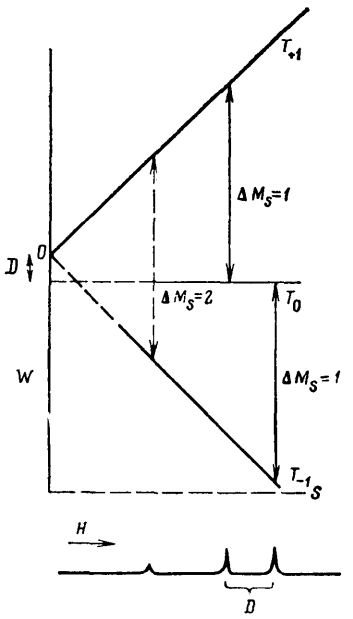


Figure 1. Energies of the states and transitions responsible for the EPR spectrum of the radical pair in a single crystal.

In the absence of axial symmetry, the degeneracy is fully removed in the zero field. The energies are then usually formulated in terms of two independent parameters D and E:

$$T_1 = 1/3D - E + g\beta H_0,$$
$$T_{-1} = 1/3D + E - g\beta H_0,$$
$$T_0 = -2/3D.$$

For radical pairs, $E \ll \frac{1}{3}D$ in most cases, and the difference between T_1 and T_{-1} in the zero field may be neglected without a significant loss of accuracy[12].

2. Determination of Spectroscopic Parameters

Determination of the fine structure parameters. The quantity $D_{\parallel}$ (i.e. D corresponding to $\alpha = 0$), the average distance between the unpaired electrons r_{av}, and the orientation of the interelectron vector of the radical pair relative to the crystallographic axes can be determined from the dependence of the fine splitting in the pair D on the orientation of the single crystals in the magnetic field.

The quantity $D_{\parallel}$ may be measured also on the basis of the EPR spectra of randomly oriented systems, which can be established experimentally in polycrystalline and vitrified specimens. The calculated line form for axial symmetry and on the assumption of a small line width is presented in Fig. 2. In the case of large line width and poorly resolved EPR spectra the rules obtained with the aid of model calculations of the line form[13] must be used in the determination of $D_{\parallel}$. When there is a significant deviation from axial symmetry, the intense "perpendicular" peaks illustrated in Fig. 2 are split by an amount $3|E|$. This usually makes it possible to determine both spectroscopic parameters (D and E). The same parameters can be found when the single crystal is rotated about two perpendicular axes after finding the principal values and directional cosines of the experimental splittings tensor in a zero field[10]. The $\Delta M_S = 1$ transition is frequently not observed in radical pairs owing to the considerable extent of the spectrum, the broadening of the lines caused by the scatter of the distances r_{av}, or very frequently, owing to the superposition of the intense signal due to isolated radicals. In this case one investigates the weak signal of the "forbidden" $\Delta M_S = 2$ transitions (Fig. 1), formally corresponding to the simultaneous reversal of two spins. The finite probability of the "forbidden" transition is due to the mixing of the T_0 and T_{+1} levels as a result of the dipole–dipole interactions; for the usual formulation of the experiment (EPR in perpendicular fields), it is given by[8]

$$\varphi = 2\frac{[D_{\parallel}^2}{H_0^2}\sin^2 2\alpha = 2\left(\frac{3g\beta}{2r_{cp}^3 H_0}\right)^2 \sin^2 2\alpha; \qquad (2)$$

when $D_{\parallel} \simeq 10^2$ G and $H_0 = 3 \times 10^3$ G, we have $\varphi \leqslant 10^{-3}$.

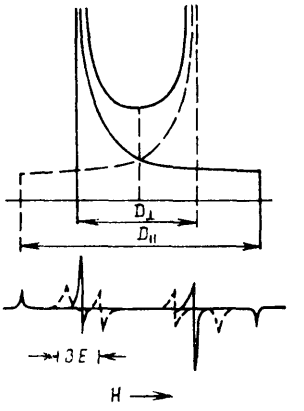


Figure 2. Theoretical EPR spectrum of polyoriented radical pairs (absorption corresponding to infinitesimal line width and the derivative of the absorption curve obtained taking into account the finite line width) for an axially-symmetrical tensor D. The additional splitting of the lines in the absence of axial symmetry ($D_{\parallel} = 2D_{\perp}$) is shown below by dashed lines.

However, the observation of "forbidden" transitions becomes possible when the line width is smaller and a higher microwave power is used[14]. The position of the centre of the $\Delta M_S = 2$ transition is determined by the condition

$$H^2 = 1/4H_0^2 - 1/3(D^2 - 3E^2),$$

i.e., when $D \ll H_0$, the position of the line virtually coincides with $H_0/2$; the shift $\delta H \simeq D^2/6H_0$ of the line may be used to determine D, but it is usually impossible to measure it.

Another method for the determination of D, proposed by Grinberg et al.[15], is based on the measurement of the shift of the saturation curves, i.e. the dependence of the signal intensity I on the amplitude of the microwave field H_1. If the spin–lattice relaxation times of the radicals and radical pairs are the same, then the I–lg H_1 saturation curves are displaced by an amount $\Delta = \lg \varphi$ (for a single-crystal), which makes it possible to determine φ and D. For polyoriented specimens, the analysis is more complicated but the simultaneous measurement of the shift Δ of the relative signal intensity $I_{\Delta M_S = 2}/I_{\Delta M_S = 1}$ frequently permits the determination of φ and D.[15]

Determination of the hyperfine structure parameters. The hyperfine interaction in the radical pairs leads to additional splitting of the levels of the triplet state ($S = 1$; $M_S = 1, 0, -1$).

$$T_1 = g\beta H_0 + 1/3D + \sum A_i M_{Ri},$$

$$T_{-1} = -g\beta H_0 + 1/3D - \sum A_i M_{Ri},$$

$$T_0 = -2/3D,$$

where the summation is carried out over all the interacting nuclei of the radical pair. Although the electronic spin moment in the triplet state is the moment of two bound electrons ($S = 1$), on average only half of this moment interacts effectively with the nuclei of each individual radical. Two electrons cannot be present in the same orbital and for this reason they occupy different normalised molecular orbitals,

$$\psi_1 = 1/\sqrt{2}\{\psi(R_1) + \psi(R_2)\},$$

$$\psi_2 = 1/\sqrt{2}\{\psi(R_1) - \psi(R_2)\},$$

formed by the combination of the orbitals of the unpaired electrons of the isolated radicals R_1 and R_2. Consequently the resulting spin density for each radical in the pair is the same as for the isolated radicals. Since the distance between the radicals is large, the magnetic cross-interaction of the nuclei of R_1 with the electrons in R_2 is negligibly small. Ultimately the splitting of the $M_S = \pm 1$ energy levels is the same as for $M_S = \pm 1/2$. For the allowed $\Delta M_S = 1$ transition, the hyperfine interaction constants for the radical pairs are equal to half the hyperfine interaction constants for the isolated radicals (Fig. 3). The same situation obtains for $\Delta M_S = 2$ transitions when the hyperfine interaction constants are expressed in magnetic field units[8].

It is noteworthy that the hyperfine interaction constants measured in "perpendicular" or "parallel" components of the spectrum of the radical pairs (Fig. 3) may refer to quite different orientations of the hyperfine interaction tensor in the magnetic field. This makes it possible to determine the orientation of the radical fragments relative to the axis of the pair.

Extent of the exchange interaction. In considering the EPR spectra we have hitherto assumed that the system is in the triplet state. In reality the triplet state of radical pairs is usually separated from the nearest singlet state by an energy gap which is very small compared with kT. All four levels are equally populated, so that 1/4 of the radical pairs do not give rise to an EPR signal. Yet another interesting case arises when the singlet–triplet splitting $E_T - E_S = J$ is greater than kT but is nevertheless fairly small and the triplet becomes thermally attainable without a significant mixing of the states. In this case it is possible to determine the exchange integral from the temperature dependence of the EPR signal intensity of the triplet state, because the signal intensity $I_{\Delta M_S = 1} \simeq 3T^{-1}\exp(-J/kT)$. The latter

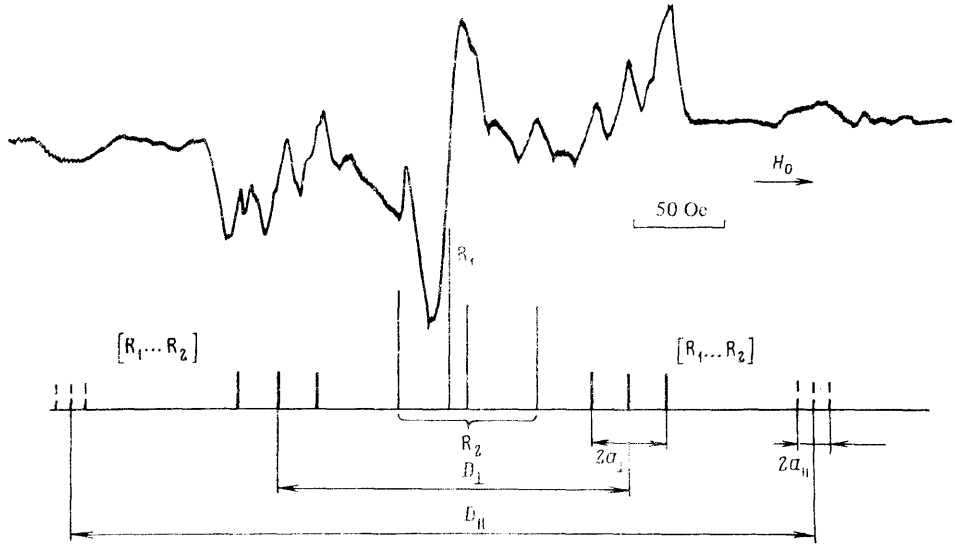


Figure 3. The real EPR spectrum of the "iminoxy–phenoxy"-radical pair and the isolated radicals in γ-irradiated polycrystalline *o*-nitrophenol and the conditions used in the interpretation of the spectrum. Evidently the hyperfine splitting in the spectrum of the radical pair is smaller by a factor of two than in the spectrum of the isolated radicals and is different for parallel and perpendicular orientations.

is of particular interest for chemistry, since the dependence of J on r_{av} determines the magnetic effects in chemical reactions [16]. The quantity J has been determined [17,18] for different values of r_{av} in radical pairs. Effects arising from the distortion of the hyperfine structure, caused by the mixing of the T_{+1} (or T_{-1}) and S_0 levels, have been used for this purpose [19,20] and not the temperature dependence of the EPR signal intensity.

3. Determination of Structural Parameters

In those cases where the point dipole approximation is valid, the dipole–dipole interaction leads to fine splitting of D in the spectrum of the radical pair described by formula (1). This formula may be replaced by an equivalent expression which is convenient for the interpretation of experimental data:

$$D = \frac{1}{2} D_{\parallel}(3\cos^2\theta \cdot \sin^2\psi - 1), \qquad (3)$$

where θ is the angle between the projection of the interelectron vector and the direction of the magnetic field H_0, ψ the angle between the interelectron vector and the axis of rotation of the crystal, and $D_{\parallel} = 55\,600/r_{av}^3$ (for resonance spins); D and $D_{\parallel}$ are expressed in gauss and r_{av} is expressed in angstroms. The crystallographic axes are selected as the axes of rotation of the single crystals. Fig. 4 presents the experimental [21] relations between D and the angle θ for pairs of iminoxy-radicals. In order to determine the positions of the detected radical pairs in the unit cell of the dimethylglyoxime crystal, parameters characterising the structures of all possible pairs of iminoxy-radicals with $r_{av} \leq 6$ Å were calculated. It was assumed [8] that the spin density is localised at the NO bond, that the electron densities at the atoms are $\rho_O = 0.67$ and $\rho_N = 0.33$, and that the same spin density distribution is maintained approximately in all the radical pairs.

The theoretical relations are compared in Fig. 4 with the experimental relations; their agreement shows quite clearly that irradiation results in the formation of all the possible types of pairs and that the distances between them are close to those in the undisrupted crystal lattice. In determining the orientations of pairs of radicals with delocalised electrons, account must be taken of the degree of delocalisation. Thus allowance for delocalisation in a pair of diphenylnitrogen radicals in tetraphenylhydrazine [18] gave values of r_{av} differing by ~1 Å from those calculated in terms of the point dipole approximation. However, in these calculations no account was taken of the form of the orbitals of the unpaired electrons. A calculation of r_{av} with allowance for the form of the orbitals has been carried out [22], which made it possible to determine the structure of the complex from which radical pairs are formed as a result of subsequent phototransfer of a proton.

4. Measurement of the Concentration of Radical Pairs

Since radical pairs have an effective spin $S = 1$ and stable radicals with $S = 1/2$ are used as the standards in EPR, account must be taken of the difference between the transition probabilities for systems with different spins. The EPR signal intensity (I) in the absence of saturation is proportional to the number of species N and to the square of the magnetic moment $\mu^2 = g^2\beta^2 S(S+1)$, i.e.

$$I \simeq NS(S+1).$$

If the specimen contains N radical pairs, then only 3/4 of them populate the magnetic (triplet) levels T_0 and $T_{\pm 1}$ (Fig. 1), and for this reason we have $I \simeq \frac{3}{2} N$ when $S = 1$. For N_R isolated radicals with $S = 1/2$, the intensity $I \simeq \frac{3}{4} N_R$. Thus, in the standard determination of concentration from EPR spectra, one obtains twice the number of radical pairs, i.e. the number of radicals combined into pairs. If no account is taken of this, one can make an error by a factor of two in the calculation of the concentration.

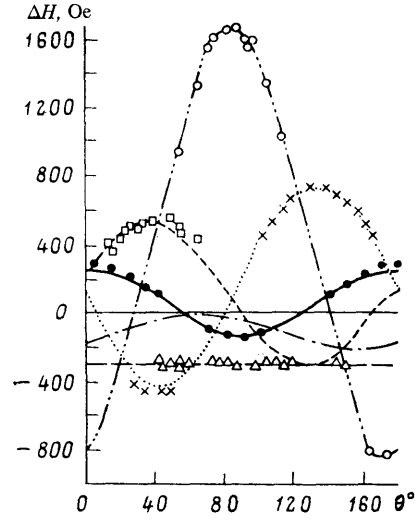


Figure 4. Experimental (circles) and theoretical (lines) angular relations for the hyperfine splitting constant D corresponding to the rotation of a dimethylglyoxime single crystal about the crystallographic a axis for five types of pairs with $r_{av} \leq 6$ Å. Comparison of the experimental points and the calculated curves makes it possible to identify the positions of the radical pairs in the unit cell of the crystal [21].

When account is taken of the differences between the transition probabilities described, the determination of concentrations from EPR spectra does not differ from the usual procedure, i.e. one compares the areas of the EPR signals of the test and reference specimens. The following useful relation has been obtained for the estimation of the area under the absorption line (s), recorded as a derivative line [23]:

$$s = kI'_{\perp}(3/2D_{\perp})^{1/2}\delta_{\perp}^{3/2},$$

where $I'_{\perp}$ and $\delta_{\perp}$ are the intensity and the apparent width of the "perpendicular" component (Fig. 5), while the shape coefficient $k \simeq 1/2$ for a Gaussian form of the individual line and $k \simeq 2$ for a Lorentzian form. A relation of the same type (but with different coefficients) makes it possible to express the area in terms of the intensity of the "parallel" component. A more accurate but cumbersome method of determining the area under the EPR signal consists in double integration or evaluation of the first moment of the experimental line.

If the usual $\Delta M_S = 1$ transition is not observed and only "forbidden" $\Delta M_S = 2$ signals are recorded, the problem of the determination of the concentration of radical pairs becomes significantly more difficult, because absolute calculations require the knowledge of the transition probability φ defined by Eqn. (2). A method has been proposed [15] for measurements based on the shift of saturation curves. In fact, for polyoriented radical pairs it is also necessary to average $\varphi(r, \alpha)$ with respect to orientations; nevertheless joint measurement of the $\Delta M_S = 2$ signal intensity and of the shift of its saturation curve relative to the signal of the radicals makes it possible to determine the concentration of radical pairs and the distance between the unpaired electrons [15].

In conclusion of the methodological part of the review, one must emphasise that the simultaneous determination of the hyperfine interaction constants and the fine structure constants, of the distance between the radicals (to within 0.1 Å), and of the orientation of the pair makes it possible to determine almost ambiguously the structure of the active centre and its position in the matrix. By studying the variation of these parameters during the course of a reaction, we have a unique possibility of investigating the "stereometry" of an elementary chemical process in a solid matrix.

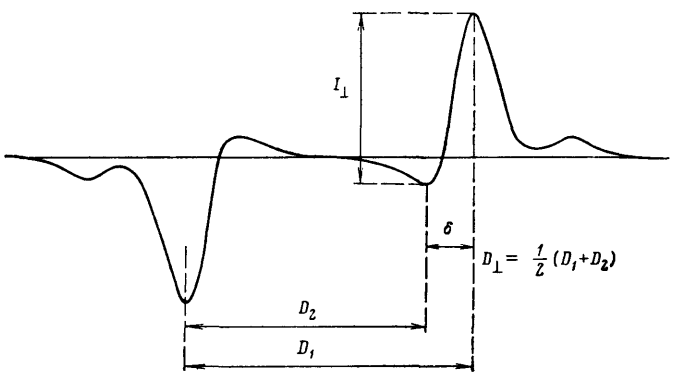


Figure 5. EPR spectrum of randomly oriented radical pairs with a large width of the individual lines and the parameters used to analyse the poorly resolved spectra [13,23].

III. THE PRIMARY STAGES IN RADIOLYSIS AND PHOTOLYSIS

In conformity with the principle of the conservation of valence, any process involving the formation of radicals from neutral molecules should proceed via a radical pair formation stage. Direct detection of radical pairs should naturally yield valuable information about the mechanisms of the reactions leading to the formation of the active centres—free radicals in solid matrices. In particular, the structure of metastable radical pairs, their orientation, and other characteristics may be used to elucidate the mechanisms of the reactions in solids under the influence of light and ionising radiation.

1. Photodissociation in the Solid Phase. Primary Steps of Photolysis

As already mentioned, in the photolysis of many solid organic compounds it is possible to detect metastable radical pairs [3,18,24]. Interesting data on the mechanism of the primary steps of photolysis have been obtained by magnetophotoselection of radical pairs. The effect of the steric selection of triplet molecules under the influence of polarised visible light is comparatively little known [25]. The magnetophotoselection effect of this kind was observed for the first time [26-28] in the formation of radical pairs under the influence of linearly polarised ultraviolet light.

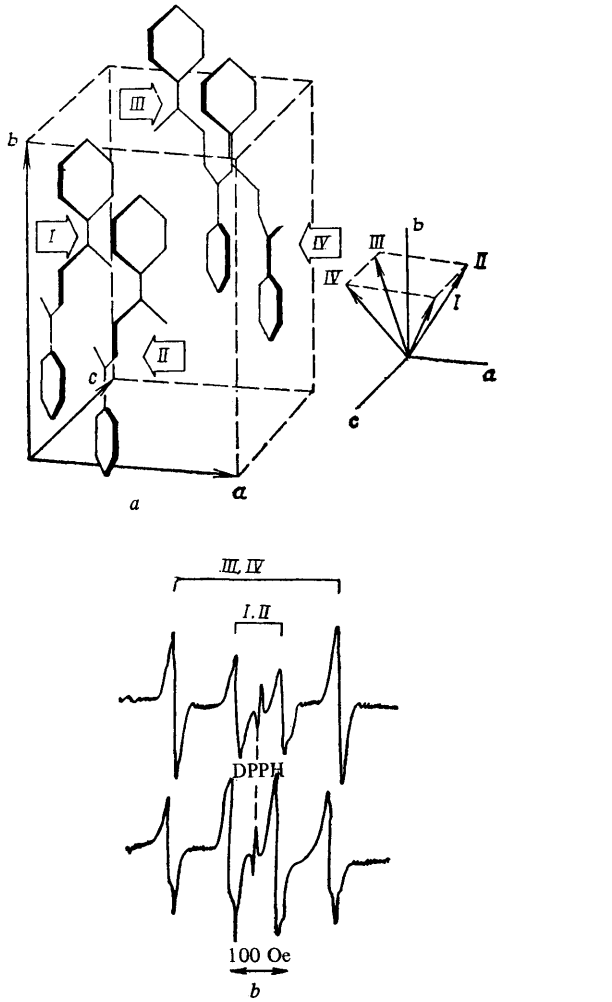


Figure 6. *a*) Schematic illustration of the orientation of different types of radical pairs in the unit cell of a benzoyl peroxide crystal; the arrows indicate the positions of the CO_2 groups evolved on photolysis [28]; *b*) selective accumulation of the EPR signals of radical pairs on photolysis with linearly polarised light: above—electric field strength $\mathbf{e} \parallel (1,\bar{1},0)$; below—$\mathbf{e} \parallel (1,1,0)$. The spectra were recorded for the $\mathbf{H}_0 \parallel (1,\bar{1},0)$ orientation.

The formation of radical pairs in acridine–acridan single crystals under the influence of linearly polarised light has been studied by EPR.[27] The directions of the dipole moments of the transitions were found from the dependence of the quantum yield of radical pairs on the angle between the electric field strength vector **e** and the crystallographic axis. In the range 250–400 nm the dipole moment of the transition is in the plane of the acridine molecule and is directed along the *c* axis; in the range 380–540 nm the component of the dipole moment of the transition is perpendicular to the plane of the molecule and is directed along the *b* axis. These results are consistent with data showing the anisotropy of the absorption of polarised light by the acridine molecule[29] and illustrate the advantages of the EPR study of the anisotropy of the absorption of light in single crystal specimens.

For benzoyl peroxide[28], the transition in the range 300–330 nm corresponds to electron transfer along the C–O bond (O is the oxygen of the peroxide bridge). The existence of four radical pairs with non-equivalent orientations in the benzoyl peroxide single crystal (Fig. 6) and the distance between the radicals, which is 5.4 Å, indicate the formation of the $PhCO_2^{\cdot}$ and $Ph^{\cdot}$ radicals on photolysis. One of the two symmetrical CO_2 groups, oriented in different ways in the cell, can be selectively abstracted by polarised light, i.e. the primary excitation is localised at one of the two symmetrical benzoxy fragments. This permitted the conclusion that there is no rapid transfer of excitation between the two equivalent fragments of the benzoyl peroxide molecule.

The analysis of the EPR spectra of polyoriented systems is more complex; nevertheless, by studying the angular distribution of the primary photolysis products (radical pairs), it is possible to determine the direction of the transition moment and the nature of the photodissociation step. Thus, for the dissociation of tetraphenylhydrazine,[26] the best agreement between the theoretically calculated EPR spectra of partly oriented radical pairs and experimental spectra was observed when the transition moment coincided with the direction of the N–N bond in the molecule and for an angle of 62° ± 3°C. It has been found analogously[30] that the vector of the electronic transition moment, excited by polarised light in 3,6-di-t-butyl-*o*-benzoquinone, is at an angle of 70° ± 5°C relative to the plane of the molecule. In both cases the polarisation of the transition corresponds to the electron transfer from the heteroatom to the benzene ring (an l–π^* transition) and the observed directions of the vectors agree with the ideas concerning the geometry of the wave functions in complex organic molecules.

The whole of the information about the structure of the radical pair and about the nature of the excitation step suggests also a mechanism for the photoinitiation of radical pairs. Thus it has been shown[27,30] that selectively excited molecules in the singlet state abstract hydrogen atoms from neighbouring molecules, forming radical pairs.

2. The Mechanism of the Radiolytic Generation of Radical Pairs

The mechanism of radiolysis is of special interest for the chemistry of elementary radical reactions, because it determines the initial steric distribution of radicals.

A large series of studies on radical pairs[12,31–36] made it possible to approach from new standpoints an understanding of the mechanism of the formation of radicals in radiolysis. However, there is no final view concerning these problems. The situation is similar as regards the question of whether the same mechanism operates in the formation of isolated radicals and radicals stabilised in a matrix in pairs and separated by short distances. Radical pairs may be formed in different ways[12,31,32]:

$$\text{I. } R_1{-}R_2 \rightsquigarrow [R_1R_2]\,,$$
$$\text{II. } [RH\ldots RH] \rightsquigarrow [RH^+RH^-] \rightarrow [R\ldots RH_2]\,,$$
$$\text{III. } [RHRH] \rightsquigarrow [RH\ldots RH]^* \rightarrow [R\ldots R] + H_2\,,$$
$$\text{IV } a.\ RH \rightsquigarrow RH^+ + e^-\,,$$
$$b.\ RH^+ + e^- \rightarrow \begin{bmatrix} R \\ R \end{bmatrix} + H\,,$$
$$c.\ RH + H \rightarrow \begin{bmatrix} R \\ R \end{bmatrix} + H_2\,,$$
$$\text{V } a.\ RH \rightsquigarrow RH^+ + e^-\,,$$
$$b.\ RH^+ + RH \rightarrow \begin{bmatrix} R \\ R \end{bmatrix} + RH_2^+\,,$$
$$c.\ RH_2^+ + e^- \rightarrow \begin{bmatrix} R \\ R \end{bmatrix} + H_2\,.$$

According to a number of data[24,31,32,37–43], it is seen that radical pairs at concentrations comparable to or greater than those of isolated radicals are generated in compounds capable of forming complexes in solutions and containing functional groups giving rise to hydrogen bonds. A probable mechanism of the formation of radical pairs may be pathway II–III, where the complex decomposes with charge transfer or excitation of the complex. A characteristic feature of this pathway is the stereospecificity in the formation of pairs, since a complex may be formed only from molecules oriented in a particular manner relative to one another in the solid phase.

The formation of radical pairs at concentrations lower by 1–2 orders of magnitude than those of isolated radicals takes place in the radiolysis of paraffins, polyolefins, and other polymers which do not contain active functional groups (for example in polyethylene[32], acrylic polymers[44], n-eicosane[45], vinyl monomers[46], etc.). This results in the formation of several types of pairs[12,35,47]. In the given instance one should consider only mechanisms IV and V, because the relaxation of molecular excitation in the condensed phase is very effective and ion-molecule processes play the main role. It has been shown[32] that the introduction of bromodecane into n-decane lowers the yield of radical pairs. The replacement of hydrogen in n-decane by deuterium has a similar influence[34]. This points directly to mechanism V. Reaction Vc may not in fact lead to the formation of an alkyl radical. If it entails the formation of RH and H, the isolated radical is stabilised by reaction IVc.

Many new characteristics of the mechanism of the formation of radical pairs have been observed in the latest studies of the low-temperature radiolysis of olefins and polymers[12,35]. It has been found that, when the radiolysis takes place at lower temperatures (1.5–4 K), then the yield of pairs exceeds that of isolated radicals and virtually all types of radical pairs which can be formed in the crystal cell are in fact formed at concentrations proportional to their statistical weight. The random formation of pairs is in poor agreement with mechanism V, where the third stage is undoubtedly stereospecific and sensitive to the distance over which H^+ or D^+ is transferred. The increase in the yield of radical pairs following the replacement of H and D and with increased length of straight-chain hydrocarbons, functioning as boundary lines limiting the free migration of H or D, also supports mechanism IV. However, the mechanism of the temperature dependence of the migration of H and D following irradiation remains incomprehensible. Similarly, it has been deduced[12,36] that there is a specific mechanism of the formation of compact pairs on the basis of the observation that the yield of pairs with a small distance between the radicals exceeds the random yield.

It has been shown[36] that irradiation with large doses at 77 K is characterised by yet another interesting feature. Despite the high overall concentration of radicals, randomly formed radical pairs are absent from the system. The concentration of pairs increases synchronously with increase of the concentration of radicals, while the formation of radical pairs should have led to the observation of a quadratic relation at higher concentrations. A "protective" mechanism begins to operate, preventing the formation of new radicals within a sphere having a radius of 10 Å around a radical which has been stabilised. In frozen solutions of stable radicals at the same concentration randomly formed pairs are stabilised at concentrations corresponding to normal statistics.

3. Steric Distribution of Radicals on Radiolysis

Data for the formation of radical pairs on radiolysis can be used to determine the complete picture of the steric distribution of radicals in irradiated solids. Studies of the role of track effects in the steric distribution of radicals, carried out by the electron spin echo method[47,48], have shown that on γ-radiolysis the overlapping of tracks begins for very low doses (~0.1 Mrad). Consequently, for the usually employed doses of 1–100 Mrad, the role of track effects may be neglected and the distribution of species throughout the specimen may be regarded as uniform. On the other hand, the data presented in the previous section demonstrated the appreciable role of pair stabilisation in the steric distribution of active centres. Furthermore, it has been shown[12,35] that, when the radiolysis is carried out at 1.5 and 4.2 K, 91% of the radicals in $C_{10}D_{10}$ are stabilised in pairs. All possible types of pairs are formed with equal probabilities from 26 nearest adjoining molecules, i.e. the distribution with respect to distances is virtually rectangular:

$$\frac{dc}{dr} = \begin{cases} 0 \text{ when } r < 2.5\text{Å and } r > 30\text{Å} \\ \dfrac{c}{r_{max} - r_{min}} \text{ when } 2.5\text{Å} < r < 30\text{Å} \end{cases}, \qquad (4)$$

where r_{min} and r_{max} determine the set of possible distances r_{av} between arbitrarily selected nearest C–H bonds. In other words, there is a random distribution in pairs. The form and width of their distribution depends on the irradiation temperature and on the isotopic concentration of the substance: with increase of temperature and following the replacement of $C_{10}D_{10}$ by $C_{10}H_{10}$, the width increases. Furthermore, in all cases the formation of pairs is accompanied by destruction and valence migration reactions[12,35] which necessitate a correction to the initial distribution. The distribution widens in the direction of higher values of r_{av} and there is partial "annealing" of pairs with small values of r_{av}. It is of interest that in polyethylene and in $C_{10}H_{10}$ the form of the distribution is independent of the dose up to 330 Mrad. The situation is different in the γ-radiolysis of dimethylglyoxime,[49] where the distribution of isolated radicals changes with increasing dose, which is manifested by an increase in the order of the recombination reaction from first to second. Thus, on low-temperature radiolysis, the radicals are initially distributed at random in pairs.

4. Conditions Governing the Stabilisation of Radical Pairs in the Matrix

The formation of radical pairs involves primarily the generation of non-equilibrium defects. Their relative stability is determined by the partial rearrangement of the molecule and the matrix. The recombination of radicals in the pair is activated even in those cases where the radical centres are nearest neighbours. The rearrangement of the matrix, stabilising the radical pairs, should seemingly cause a scatter of the parameters of the radical pairs (the distance r_{av} and orientation). However, the EPR spectra of radical pairs described in the literature indicate a surprising constancy of the distance between the radicals. For the $Ph^{\bullet}...CH_3^{\bullet}$ pair, it is possible to record a hyperfine splitting of the β-protons of the phenyl radical with a constant of 3 G.[24] This implies that the scatter of the parameters should be less than 3 G, i.e. less than 3% and the scatter of r_{av} should be less than 1%, i.e. 0.06 Å. A similar situation obtains if one assumes also a greater scatter of r_{av} but with a sharp extremum at $r = 6.2$ Å.

The pairs of iminoxy-radicals arising in dimethylglyoxime single crystals on radiolysis at 77 K have structural parameters close to those in the undamaged structure of the crystal[21]. Even when "large" water molecules are evolved in the formation reaction[50], the scatter of the distances is less than 1%. However, in this case a broad background line is generated and probably includes the spectra of the radical pairs stabilised in the defect regions with several different distances between the radicals, i.e. a distribution with respect to r_{av} with a sharp extremum is observed. In glassy solutions the stabilisation conditions must reflect the inhomogeneity of the matrix structure. Thus the EPR spectra of allowed transitions in frozen solutions of certain acyl peroxides[51] are more broadened, apparently owing to the presence of a distribution with respect to r_{av}. Tetraphenylhydrazine, where radical pairs with fixed distances between the radicals are observed even in frozen solvents, is an interesting example. The sterically branched tetraphenylhydrazine molecules probably generate a solvent structure in their vicinity. On the other hand, in the decomposition of "ribbon" molecules, which generate a solvent structure less effectively, a distribution with respect to r_{av} is generated.

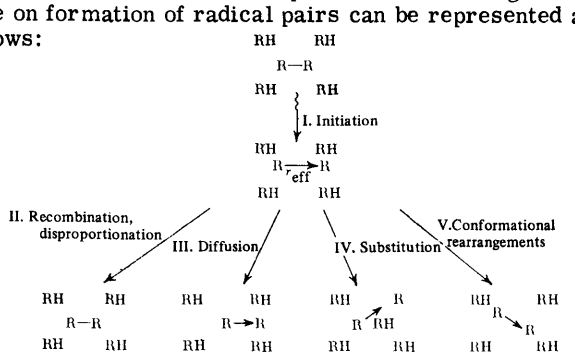
An intermediate case between pair formation in the decomposition of a single molecule, on the one hand, and the formation of pairs from two neighbouring molecules is pair generation from "weak" binary complexes[52]. In this case a rectangular distribution [Eqn. (4)] is observed with respect to the distances between the radicals in the pair with $\Delta r = r_{max} - r_{min} = 0.2$ Å. This feature of pair stabilisation has been used to investigate the geometry of the formation of binary complexes—the precursors of radical pairs. The structure of the binary complex of 3,6-di-t-butyl-*o*-quinone with 2,4,6-tri-t-butylphenol, formed on mixing these compounds, has been determined[22] from the EPR spectra of the radical pairs formed on photolysis. The pair stabilisation conditions determine the stereochemistry and kinetics of thermal radical reactions, which are considered in the next section of the review.

IV. THE KINETICS OF ELEMENTARY REACTIONS IN THE "CAGE"

One of the most significant features of solid-phase reactions is the limited mobility of the reacting species or species formed as a result of the reaction. For this

reason, the solid may be represented, with an adequate degree of approximation, as a body consisting of compartments ("cages") containing immediately adjoining molecules; the compartments do not interact with one another and for this reason do not average out the properties of the system. The data at present available for the kinetics of solid-phase radical reactions show that virtually all the characteristics of the processes are already manifested on a scale corresponding to a single cage. A radical pair trapped in the cage serves as the ideal probe for the direct measurement of the kinetic constants of elementary reactions in the solid phase. This section reviews the results of such measurements and discusses certain specific conclusions concerning the mechanisms of solid-phase reactions based on them.

The overall mechanism of processes occurring in the cage on formation of radical pairs can be represented as follows:



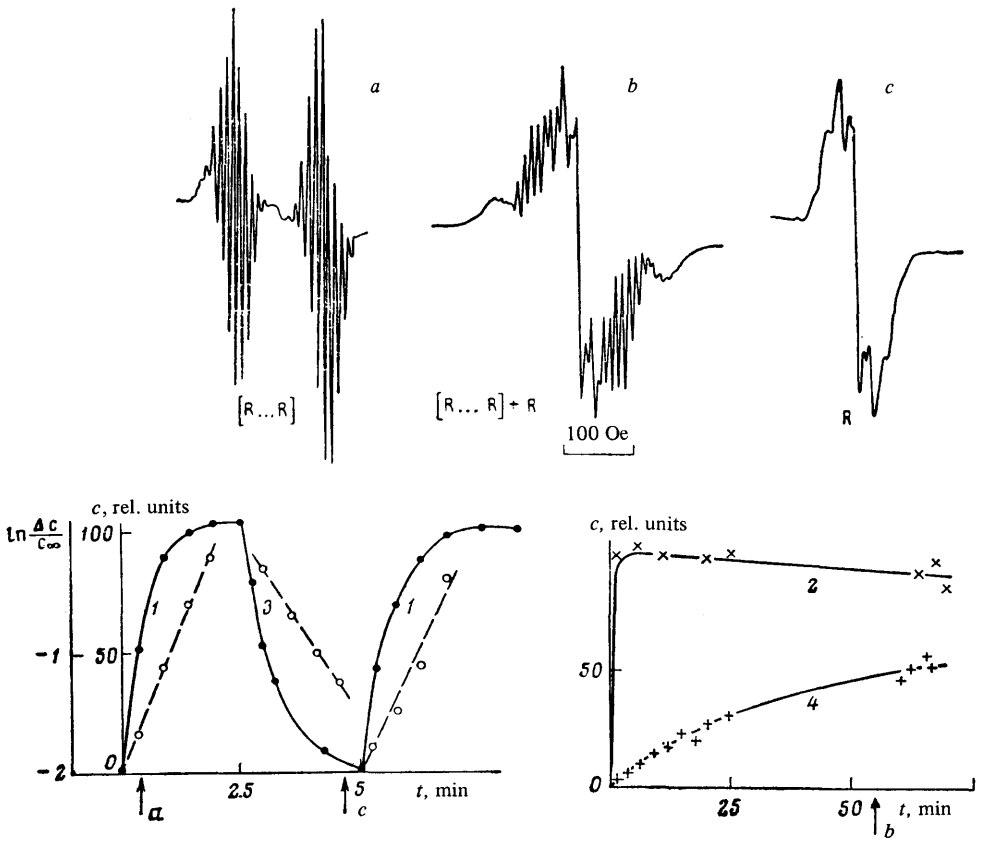


Figure 7. Kinetics of the accumulation (curves *1* and *2*) and destruction (curve *3*) of radical pairs and the accumulation of radicals (curve *4*) in the photolysis of azobisisobutyronitrile at 77 K. The linear forms of the kinetic curves are illustrated by dashed lines in terms of the variables corresponding to an exponential radical destruction law: above—EPR spectra at the instants indicated by arrows on the abscissa axes.

Depending on the ratio of the rate constants for different steps, a particular reaction pathway obtains in each specific system. On photolysis the radical pairs formed largely recombine or disproportionate in the cage and a simplified reaction mechanism can be represented as follows:

$$M \overset{k_0}{\rightsquigarrow} [R_1 \ldots R_2] \overset{k_2}{\rightarrow} R_1 + R_2 \quad . \qquad (5)$$
$$\underset{M'}{\overset{k_1}{\downarrow}}$$

The radical pairs produced on radiolysis are usually stable at the initiation temperature and on heating it is possible to investigate independently processes II, IV, V. When pairs of stable radicals are used, it is convenient to investigate diffusion processes III.

1. Recombination and Liberation from the Cage

The study of "live" metastable radical pairs, formed on photodecomposition of unstable organic compounds, is of considerable interest for understanding the mechanism of initiation in the solid phase.

On the basis of the simplest mechanism (5) of the photodissociation of molecules in the cage, it is easy to obtain the following expressions from the kinetics of the accumulation of radical pairs (without taking into account the subsequent reactions of isolated radicals):

$$c_{RR} = c_\infty \{1 - \exp[-(k_1 + k_2)t]\},$$
$$c_R = \frac{k_2}{k_1 + k_2} c_\infty \{(k_1 + k_2)t - \{1 - \exp[-(k_1 + k_2)t]\}\}, \qquad (6)$$

where $c_\infty = k_0 c_M/(k_1 + k_2)$. It follows from Eqns. (6) that an induction period, approximately equal to the lifetime of radical pairs, should be observed in the accumulation of radicals and that a steady radical accumulation rate should be established subsequently:

$$w_R = k_0 c_M k_2/(k_1 + k_2) = f k_0 c_M,$$

where f is the probability of liberation from the cage. Since the initial rate of accumulation of radical pairs $w_{R\ldots R} = k_0 c_M$, it is possible to find the probability of liberation from the cage on the basis of the ratio of the slopes of the linear sections of the experimental curves, while measurements of the absolute rate and the analysis of the radical pair accumulation or destruction curve make it possible to determine all the kinetic constants in Eqns. (5). Experiments of this type have been carried out on the photodecomposition of solid organic initiators—azobisisobutyronitrile,[3,53] azobis-3-methyl-2-phenylbutane,[54,55] tetraphenylhydrazine,[18,24] and a number of acyl peroxides[24,51] At low temperatures (77–100 K, sometimes up to 150 K) EPR spectra can be recorded for crystalline substances and frozen solutions. Some of the results of the kinetic studies are illustrated in Fig. 7. The signal intensities in Fig. 7 are quoted in relative units but account is taken of the shape coefficients of the spectra, so that the values of c_R and $c_{R\ldots R}$ are proportional to the true concentrations. We thus find from Fig. 7 that $f = 2 \times 10^{-2}$ at 77 K for crystalline azobisisobutyronitrile. This value is much less than that obtained from kinetic measurements in solution ($f = 0.5$ according to Kulitski et al.[56]), but is in good agreement with $f = 3 \times 10^{-3}$ calculated for the initiation of polymerisation in the solid phase[57].

Fig. 7 shows that the radical pair accumulation and destruction kinetic curves can be expressed in a satisfactory linear form in terms of semilogarithmic coordinates, i.e. the destruction of radical pairs is indeed a first-order reaction. The rate constant for the destruction of radical pairs in the "cage" in crystalline azobisisobutyronitrile has been measured[58] over the range 63–77 K. Further measurements have been made in tetraphenylhydrazine single crystals. The constants are compiled in the Table.

Kinetic curves for radical pairs and radicals formed in the photolysis of acetylbenzoyl peroxide have been published[51]. The radical accumulation curve shows a distinct inflection associated with the lag in the formation of radicals, in conformity with Eqn. (6). This implies that radical initiation precedes the appearance of isolated (in the given instance methyl) radicals, but the induction period is clearly shorter than the time required for the establishment of a steady-state concentration of radical pairs, i.e. the reaction mechanism is apparently more complex than that described by Eqns. (5).

In the study of processes of the type described the problem naturally arises whether the recombination reactions and the reactions involving liberation from the cage are thermal or whether they are also associated with photoexcitation. In the case of azobisisobutyronitrile the time constants for photoaccumulation and destruction in the dark are the same (Fig. 7), which indicates a thermal mechanism of the recombination reaction. On the other hand, in the case of acyl peroxides, direct data have been obtained indicating the influence of light on the liberation from the cage. For example, when peroxydisuccinic acid is irradiated with light at wavelengths in the range 240 to 400 nm, radicals and radical centres accumulate rapidly, but only pairs are produced in the presence of light corresponding to the 330–570 nm band[51]. The radical pairs in peroxydisuccinic acid are converted into radicals even under the influence of visible light[51]. The kinetics of the destruction of radical pairs formed in the low-temperature photolysis (77 K, 300–400 nm) of mono- and poly-crystalline tetraphenylhydrazine specimens and frozen solutions of tetraphenylhydrazine in toluene have been studied in detail[59,60]. In single crystals the destruction of radical pairs obeys the equation for first-order kinetics. In powders and vitrified solutions the kinetics are of the "stepwise" type, which corresponds to a set of kinetic constants (see Table) with a rectangular distribution with respect to E having a width $\Delta E = 2.3 \pm 1$ kcal mole^{-1} and $\lg k_0 = 12.1 \pm 3$ s^{-1}. Vitrified solutions of tetraphenylhydrazine are interesting in view of the similarity of the experimental conditions to those which really obtain when compounds of this class are used as initiators. It has been shown[60] that the probability of the liberation of radicals from the cage and hence the efficiency of the initiator are negligibly small in the vitrified crystalline state and that the probability is close to unity in the region corresponding to the devitrification of the solution.

In those cases where the reactions take place in the region remote from the phase transition temperatures, the reaction in the cage becomes strongly stereospecific. A set of studies in this field was undertaken by McBride and coworkers[53–55,61]. When asymmetric fragments recombine, the composition of the products is not random but depends on the structure of the cage. Thus in the case of crystalline azobisisobutyronitrile 95% of the photolysis products are formed via radical pairs in undisrupted regions of the crystal and only ~5% may be formed on defects, giving rise to other compounds[61]. In the liquid phase the ratio of product yields is reversed. A study of

the photolysis of acetylbenzoyl peroxide has shown that even at low temperatures the products are not just a pair of benzoyloxy- and methyl radicals but also (as a result of decarboxylation) a "phenyl-methyl radical" pair. This gives rise to a large set of recombination products which may be formed in the cage. However, the structure of the cage facilitates the interaction of the methyl radical with oxygen forming part of the peroxide chain before decomposition, which leads to the selective formation of products[51].

2. Substitution and Disproportionation Reactions in the Cage

At low temperatures, where the diffusional mobility of large molecules is frozen, reactions of the type

$$R + RH \rightarrow RH + R, \qquad (7)$$

which are capable of ensuring the migration of the valence over considerable distances, acquire particular importance. Such reactions may occur both on heating and under the influence of light. However, direct measurement of the kinetic constants for reaction (7) became possible only when radical pairs were used, because there is no change in chemical structure during the reaction and only the coordinate of the active centre is altered. Reactions of type (7) were first investigated in detail in γ-irradiated dimethylglyoxime and {[D_2]dimethylglyoxime [31,62]}. The rate constants, the kinetic isotope effects, the direction of migration, and hydrogen migration distances were measured. The experimental results are presented in Fig. 8 and in the Table. A characteristic feature of the thermal valence migration reactions is their stereospecificity—the anisotropy of the directions of valence migration. The sensitivity of reactions to weak intermolecular interactions is a no less interesting feature. Thus it has been observed[31] that at low temperatures (77–120 K) intramolecular migration of hydrogen via one of two pathways, equivalent as regards the direction in the crystal, the distance traversed, and the chemical structure of the radical fragments, is observed. It is apparently due to the ability of iminoxy-radicals to form hydrogen bonds with the molecules of the medium or with one another.

In those cases where there are no interactions of this kind or their energy is low compared with the activation energy for the migration reaction, a dynamic equilibrium is observed between two positions of the active centre. In dimethylglyoxime[31] such migration reactions are observed at higher temperatures (270–320 K). There is intermolecular migration of a hydrogen (deuterium) atom, which can be located in two closely adjacent positions with equal probabilities; this is manifested when the EPR spectra of two types of radical pairs are recorded. A similar behaviour has been observed in studies[30,52] of the photolysis of frozen solutions of 2,4,6-tri-t-butylphenol and 3,6-di-t-butyl-*o*-benzoquinone, which form a weak complex (see Section III). The transfer of a hydrogen atom from phenol to quinone leads to the formation of radical pairs of two types, which arise owing to the intramolecular exchange between the two carbonyl groups of *o*-quinone.

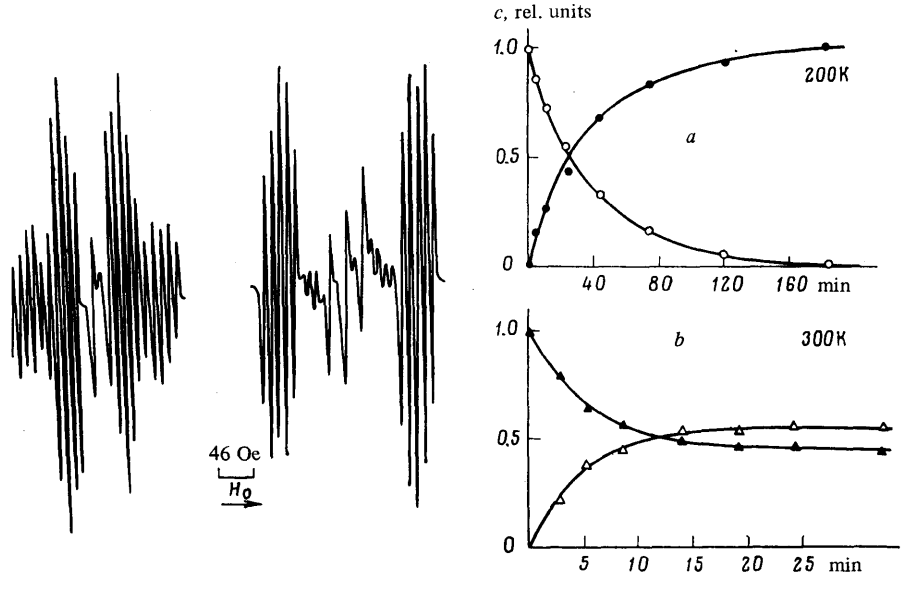
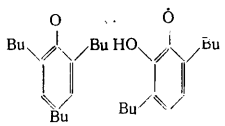
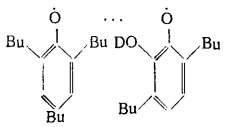
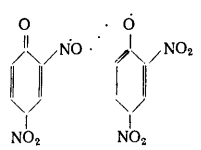
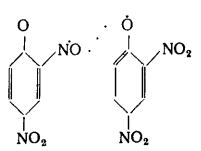


Figure 8. Kinetics of intramolecular (*a*) and intermolecular (*b*) substitution reactions (R...HR) → (RH...R) in γ-irradiated [D_2]dimethylglyoxime (*a*) and non-deuterated dimethylglyoxime (*b*): on the left—transformation of the EPR spectra of the radical pairs in the course of the intramolecular substitution[31].

The rate constants for elementary radical processes determined from the EPR spectra of radical pairs.

Structure of radical pair	r_1, r_2, Å	Phase state	Elementary process	Parameters	ΔT, K	Refs.
			Azobisisobutyronitrile			
R...N≡N ... R, where R=$(CH_3)_2C(CN)$	r_1=5.6	Single crystal	Recombination	E=3.5±0.6, $\lg k_0$=8	63—77	3
»	r_1=5.6	Single crystal	Recombination	E=5.0; $\lg k_0$=11	72—77	35
»	r_1=5.6	Single crystal	Liberation from cage	f=(2±1)·10^{-2}	77	3
			Tetraphenylhydrazine			
$Ph_2\dot{N}$ $\dot{N}$	r_1=4	Single crystal	Recombination	E=7.0±0.5; $\lg k_0$=8.4±0.8	130—150	59
»	r_1=4	Crystallised solution in toluene	Recombination	E_{min}=5.4±1.5; E_{max}=7.7±2.2; $\lg k_0$=12.1±3	77—130	59
»	r_1=4	Vitrified solution in toluene	Recombination	E_{min}=5.2±1.5; E_{max}=7.5±2.0; $\lg k_0$=11.6±3	77—110	60
»	r_1=4	Devitrification region	Liberation from cage	$E\simeq$30; $\lg k_0\simeq$70; $f\geqslant$0.1	110—120	60
			Dimethylglyoxime			
HONPNO'...'ONPNOH, where P=$C_2H_5(CH_3)_2$	r_1=5.4	Single crystal	RH+R→R+RH	E=1.40±0.07; $\lg k_0$=0.10±0.16	77—110	31
DONPNO'...'ONPNOD	r_1=5.4 r_2=5.5	Single crystal	RD+R→R+RD	E=7.4±0.1: $\lg k_0$=4.5±0.1	190—200	31,62
HONPNO'...'ONPNOH	r_1=5.6 r_2=6.1	Single crystal	RH+R$\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}$R+RH	E=17.7±0.7; $\lg k_0$=10.5±0.6; k_{12}/k_{21}=1.4±0.2	270—310	31,62
DONPNO'...'ONPNOD	r_1=5.6 r_2=6.1	Single crystal	RD+R$\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}$R+RD	E=24.2±0.4; $\lg k_0$=13.2±0.3; k_{12}/k_{21}=1.4±0.2	310—340	31,62
HONPNO'...'ONPNOH	r_1=5.6 r_1=6.1	Single crystal	Disproportionation	E=21.5±0.9; $\lg k_0$=10.8±0.6	300—340	31,62
DONPNO'...'ONPNOD	r_1=5.6 r_1=6.1	Single crystal	Disproportionation	E=22.1±0.9; $\lg k_0$=11.3±0.6	300—340	31,62
			Complex of 2,6-di-t-butyl-*o*-benzoquinone and 2,4,6-tri-t-butylphenol			
	r_1=5.15 r_1=6.25	Vitrified solution in liquid paraffin	Disproportionation	E_{min}=6.7±1; E_{max}=10±1; $\lg k_0$=8±2	130—200	52
	r_1=5.15 r_1=6.25	Vitrified solution in liquid paraffin	Disproportionation	E_{min}=11±1; E_{max}=17±1; $\lg k_0$=13±2	130—200	52
			2,4-Dinitrophenol (OH)–2,4-dinitrophenol (OD)			
	r_1=5.18 r_2=4.8	Polycrystalline substance (OH)	Rearrangement of CNO fragment	E=9.4±0.2; $\lg k_0$=8.7±0.2	160—190	81
»	r_1=5.18 r_2=4.8	Polycrystalline substance (OD)	Rearrangement of CNO fragment	E=9.5±07; $\lg k_0$=8.1±0,8	160—190	81
»	r_1=4.8 r_2=4.68	Polycrystalline substance (OH)	Rotation of radical as a whole	E=9.8±1.5; $\lg k_0$=6.6±1.6	200—240	81
»	r_1=4.8 r_2=4.68	Polycrystalline substance (OD)	Rotation of radical as a whole	E=9.7±1.3; $\lg k_0$=6.7±1.3	200—240	81
	r_1=4.68	Polycrystalline substance (OH)	Recombination	E_1=18.7±0.8; $\lg k_{01}$=12.0±0.6 E_2=22.4±0.5; $\lg k_{02}$=13.4±0.5	270—310	81
»	r_1=4.68	Polycrystalline substance (OD)	Recombination	E_1=27.5±2.5; $\lg k_{01}$=17.2±1.9 E_2=29.6±6.5; $\lg k_{02}$=18.3±4.8	270—310	81

Notation: r_1 and r_2 are the distances between the radicals before and after the process, E (kcal mole^{-1}) and k_0 (s^{-1}) are the Arrhenius parameters of the rate constant, f is the probability of liberation from the cage, ΔT is the temperature range, and E_1, k_{01}, E_2, and k_{02} are the parameters for low and high degrees of conversion respectively.

Under the influence of ultraviolet light, migration reactions are also observed in γ-irradiated dimethylglyoxime crystals at 77 K.[63] However, they are non-stereospecific and proceed via several pathways simultaneously. Irradiation with light apparently leads to electronic excitation of the radicals, which react in the excited state either with a neighbouring radical (destruction of the pair) or with a neighbouring molecule (valence migration).

Disproportionation reactions have much in common with valence migration reactions of type (7). As a rule, they exhbiit a kinetic isotope effect[31,52,62]. The stereochemistry of the disproportionation of radical pairs has been examined[57] and it has been shown that the pathway followed in the transfer of hydrogen from the quinone radical to the phenone radical during "annealing" does not coincide with the channel in phototransfer or during formation. The rate of reaction is then extremely sensitive to the distance traversed and a distribution with respect to distances leads to a distribution with respect to rate constants.

3. Characteristics of the Kinetics of Elementary Reactions in the Cage

The kinetic constants found from the EPR spectra of the radical pairs are compiled in the Table. Evidently even in those cases where the reaction is elementary, i.e. the kinetics satisfy a first-order equation, the Arrhenius parameters differ sharply from the "usual" values for analogous reactions in the gas and liquid phases. In vitrified and powdered matrices the reaction kinetics are "polychromatic" and are described by a spectrum of kinetic constants. These features are in general characteristic of the kinetics of radical reactions in solids[59,64-67] and are apparently of key importance for the understanding of their mechanism. For radical pairs, it is possible to achieve the closest approach to the elementary stages of the process. It will be shown below that in many instances this has made it possible to understand the nature of the observed phenomena.

Tunnel transfer of hydrogen. From the kinetic point of view, rapid thermally activated migration reactions, occurring in dimethylglyoxime at low temperatures, are of particular interest. The measured dependence of the rate constants on temperatures obeys the Arrhenius equation. However, the pre-exponential factors for unimolecular reactions vary over a wide range, from several reciprocal seconds (for a reaction at the temperature of liquid nitrogen) to normal values of 10^{13} s^{-1} at 300 K, and there is a linear compensation relation between $\lg k_0$ and E. The migration reactions investigated are characterised by considerable kinetic isotope effects. Low pre-exponential factors for the low-temperature reactions and the anomalously large kinetic isotope effect indicate a tunnel reaction mechanism. If the rate of the process is estimated in terms of the reaction [RH...R] → [R...HR] for a continuous distribution of the vibrational levels of the bond being ruptured, then the experimental points corresponding to a barrier half-width $d_{1/2}$ = 0.6 Å, E_H = 15 kcal $mole^{-1}$, and E_D = 16 kcal $mole^{-1}$ fit satisfactorily on theoretical curves (Fig. 9). In order to illustrate the relation between the true and apparent activation energies, "Arrhenius" straight lines have been drawn through the experimental rate constants in Fig. 9. Evidently the unjustified linear extrapolation yields in this case unduly low values of E and k_0 and for deuterated dimethylglyoxime higher pre-exponential factors correspond to higher values of E, i.e. a compensation effect is observed. Subsequently the occurrence of hydrogen transfer via a tunnel mechanism at low temperatures was confirmed by numerous experimental investigations (see the review of Lebedev et al.[69]).

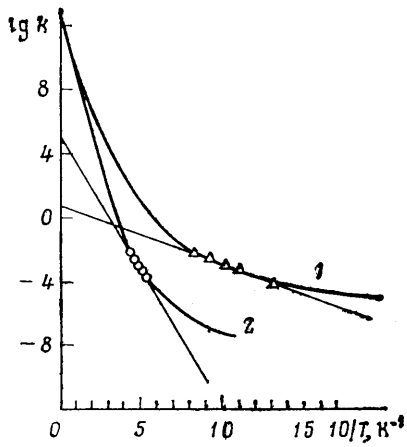


Figure 9. Calculated and experimental temperature dependences of the rate constants for the reaction (R...RH) → (RH...R) in dimethylglyoxime (curve *1*) and [D_2]dimethylglyoxime (curve *2*). The calculation was carried out taking into account the tunnel transitions for the quasi-continuous distribution of the vibrational levels of the dissociating bond corresponding to a barrier half-width $d_{1/2}$ = 0.6 Å and barrier heights E = 15 and 16 kcal $mole^{-1}$ respectively[62]. Evidently in the temperature range of the measurement it is possible to draw straight lines through the experimental points, whose slope yields the apparent activation energy $E_{eff} \ll E$.

Polychromatic reactions. In most radical reactions occurring in the solid phase at low temperatures, a kinetic arrest of the reaction (i.e. a sharp reduction of its rate) is observed for a certain degree of reaction. The stepwise nature of the recombination is usually accounted for by the fact that the reacting centres are non-equivalent and that a set of reaction rates obtains. Several hypotheses explaining such distribution of properties have been put forward[64-67,69]: (a) structural inhomogeneity of the specimen; (b) the presence of a distribution with respect to the distances between the reacting species; (c) an increased local concentration of radicals at the sites of defects; (d) thermal chain recombination†. The last two possibilities are known to be negligible for radical pairs. The distribution of properties in the case under consideration may be due either to the structural inhomogeneity of the specimen or to the stabilisation of radicals separated by different distances.

†Thermal chain recombination is the chain destruction of free radicals activated by the energy liberated in the elementary recombination step.

A correlation has been observed[34] between the distance in the radical pair obtained on γ-radiolysis of $C_{10}D_{22}$ and their destruction temperature. It has been possible to establish directly[52] the relation between the rate constant (activation energy) for the reaction and the distance between the reacting radicals in the cage. In frozen solutions of quinones and phenols a change in the parameter D, i.e. in the distance between the radicals, was observed in the course of the stepwise "annealing" of radical pairs, associated with the disproportionation of radicals in the cage. An increase of D by 0.2 Å corresponded to an increase of the activation energy for the reaction by 3.3 kcal mole^{-1}. In polycrystalline n-decane the variation of the distance between the radicals in the course of their recombination was investigated by the method involving the saturation of forbidden transitions (Fig. 10). It has been shown[36] that the activation energy for recombination increases approximately linearly with distance in the range 6–8 Å.

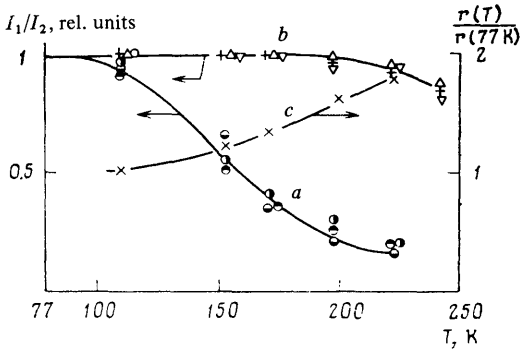


Figure 10. "Annealing" of the EPR signals of radical pairs (*a*) and isolated radicals (*b*) in γ-irradiated polycrystalline n-decane; *c*) variation of the minimum distance between the radicals during "annealing". Analysis of curves *a* and *b* shows that the effective activation energy for the recombination reaction increases linearly with distance[36].

However, the scatter with respect to distances is not the only cause of the existence of a set of rate constants for the reaction in the cage. In many instances the stepwise reaction is not accompanied by a change in the parameter D. This implies the existence of kinetically non-equivalent cages owing to a difference in the immediate environments of the reacting molecules. The direct influence of the inhomogeneity of the matrix on the reaction kinetics has been demonstrated[67,70]. It has been shown that in oriented polyethylene the kinetics of the destruction of a radical pair with $r_{av} = 5.3$ Å, studied on the basis of the spectrum of an allowed transition, are distinctly "stepwise" and the scatter of the constants is very wide. This observed feature has been followed consistently in experiments using tetraphenylhydrazine[59,60] where the recombination of pairs with the same distances between the radicals in single crystals obeys a simple first-order law, while in vitrified and crystallised solutions and in crystalline tetraphenylhydrazine powder the destruction kinetics become stepwise (Fig. 11). The results described demonstrated probably for the first time that the stepwise kinetics of solid-phase reactions are due to the scatter of the properties of the medium at the level of the kinetic cage.

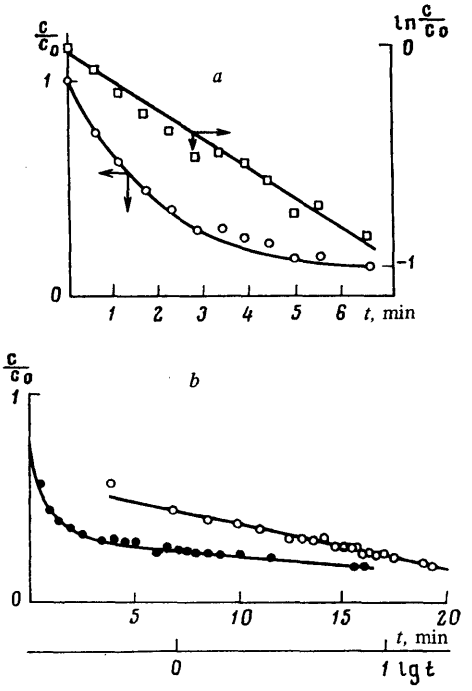


Figure 11. Kinetics of the "merging" of the radical pairs in single crystals (*a*) and in a polycrystalline solution of tetraphenylhydrazine in toluene (*b*). In the former case the kinetic curve is described by an exponential function and in the latter by a linear relation with lg t, which indicates the existence of a broad spectrum of rate constants[59].

The existence of cages with different immediate environments in vitrified solutions is not particularly surprising. However, the stepwise nature of the destruction of radical pairs in powdered specimens requires special consideration. The four types of radical pairs formed in the decomposition of four molecules with different orientations are magnetically non-equivalent in tetraphenylhydrazine crystals. In polycrystalline specimens the pairs are spectroscopically identical, but the exponential kinetics of the destruction of radical pairs of each type are characterised by different rate constants[59]. By measuring the overall concentration of pairs of all types, we can observe complex first-order kinetics—stepwise destruction. An analogous behaviour has been observed in the "annealing" of radical pairs in 2,4-dinitrophenol. Analysis of the spectra revealed two sets of magnetically non-equivalent radical pairs and the destruction kinetics

in powders became satisfactorily linearised on the assumption that there are two exponential destruction rate constants. Thus the ĒPR spectra of radical pairs in crystalline solids allow the resolution of kinetically non-equivalent states of radical pairs (with a fixed distance). This makes it possible to investigate the relation between the structure of the cage and its dynamic properties.

V. CONFORMATIONAL AND MOLECULAR MOBILITY IN SOLID MATRICES

The data described above confirm that the reactions in solid matrices are controlled by or at least depend strongly on molecular motions in the cage. For this reason, the simultaneous investigation of elementary molecular motions (translational displacement, rotation, reorientation, and conformational rearrangements) and chemical reactions is a very important task. The spin probe method [71-73] is not very effective for such purposes, since in most cases the reactions are "unfrozen" at very low frequencies of molecular motions when the EPR spectra of the paramagnetic label of the probe do not yet show any changes. The recombination-kinetic method [65] permits the detection of slow molecular motions but it yields only indirect information about the elementary motions, since it is based on the measurement of the rate of the overall recombination of radicals. The use of radical pairs as two-spin probes in the matrix leads to the possibility of the direct investigation of the dynamics and stereochemistry of slow molecular motions.

1. The Study of Phase and Structural Transitions

For compact radical pairs, the recombination of active centres does not require translational diffusional displacements and pair labels are presumably extremely sensitive to local molecular motions. It has been shown [74] that the different stabilities of radical pairs in polymers are of interest from the standpoint of the detection of phase and structural transitions (Fig. 12). Fig. 12 shows that the heating curve for $\Delta M_S = 2$ signals has inflections indicating structural changes in the polymer, i.e. phase transitions slightly "modulate" the curve for the distribution of the pair recombination activation energies. Inferences can be drawn about the structural and phase transitions by measuring the distances between the radicals r_{av} over a wide range of temperatures for any type of pairs which are stable at high temperatures. In the absence of transitions a dependence reflecting simply the linear expansion of the crystal will be obtained [75].

2. Translational Mobility

The frequency of translational motion can be determined directly from the EPR spectra of radical pairs because the liberation of the radical from the cage and its migration over a distance corresponding to one cage diameter lead to the disappearance of the spectrum of the radical pair and to the appearance of signals due to the isolated radicals. The kinetics of the liberation of the diphenylnitrogen radical from the cage have been investigated [60] for the devitrification of frozen solutions in toluene. The characteristic times of the liberation of the radical from the cage $\tau \simeq 10$ s makes it possible to estimate the frequency of translational motion in the liquid phase $\nu_{tr} \geqslant 10^{-1}\ s^{-1}$. To refine the estimate, the EPR spectra of frozen solutions of the stable 2,2,6,6-tetramethyloxopiperidin-1-yloxy-radical in toluene were recorded. Since a change in the form of this spectrum was not observed on devitrification, the upper limit to the rotational frequency is $\nu_{tr} < 10^{8}\ s^{-1}$.

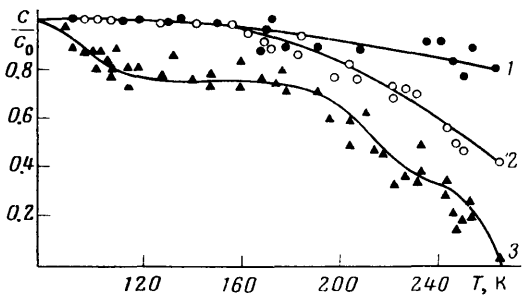


Figure 12. Heating curves for alkyl radicals (curve *1*), a mixture of alkyl and peroxy-radicals (curve *2*), and radical pairs (curve *3*) in polyethylene. The inflection points in the range 160–260 K correspond to structural transitions in the crystalline phase [74].

Yet another interesting possibility of investigating elementary translational motions arises when one employs the stable radical pairs formed as a result of the random entry of radicals into a single cage on dissolution of nitroxy-radicals at high concentrations (0.01–0.1 M). [76] The $\Delta M_S = 2$ transitions at half field (see Section II) are then distinctly observed despite the existence of a more intense $\Delta M_S = 1$ signal due to the isolated radicals.

When the translational mobility is "unfrozen", the number of pairs of chemically stable radicals remains unchanged and is statistically determined, though the lifetime of an individual pair diminishes, since it is determined by the average residence time of the radical in a "settled" position, i.e. the correlation time for translational motion τ_{tr}. This leads to the modulation of the values of r_{av} and α, and, in conformity with Eqn. (2), to the modulation of the intensity of the $\Delta M_S = 2$ transition with a frequency τ_{tr}^{-1}. As a result, the EPR line should become broadened by an amount $1/\gamma_{tr}$, i.e. it becomes possible to measure the frequencies of the translational jumps executed by the radical [78]. A rigorous calculation of the line form fully confirmed this simple picture [77].

A study has been made [76] of the EPR spectra of solutions of 2,2,6,6-tetramethylpiperidinyl-1-oxy-radicals in liquid paraffin and toluene at a concentration of $(1-5)(1-5) \times 10^{19}\ cm^{-3}$. The temperature variation of the EPR signal is illustrated in Fig. 13. Evidently the intensity of the forbidden transition diminishes, but the line width hardly increases. Such behaviour of the line cannot be accounted for within the framework of relaxation theory [77] and indicates the existence of a set of very different frequencies of translational motions τ_{tr}^{-1}. In this case the $\Delta M_S = 2$ signal represents, as it were, a superposition of lines with very different widths; only the narrowest line, corresponding to the signal due to cages where the jump frequency is a minimum, is recorded. Thus polychromatic kinetics are characteristic not only of chemical

reactions but also of elementary motions in the solid. This agrees well with the model of kinetically non-equivalent cages, which is nowadays resorted to for the interpretation of a wide variety of processes in the solid phase[65-67,69].

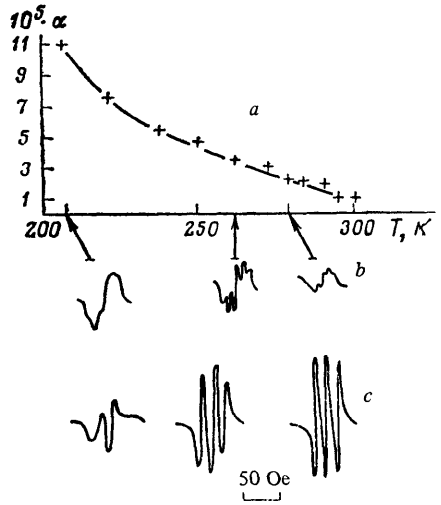


Figure 13. Temperature dependence of the relative intensity (*a*) and form of the EPR spectrum (*b*) for the $\Delta M_S = 2$ transition involving stable radical pairs in liquid paraffin; *c*) EPR spectra of single crystals ($\Delta M_S = 1$). The decrease of the $\Delta M_S = 2$ signal intensity without an increase in line width indicates the presence of a broad spectrum of frequencies of the translational displacements of radicals[76].

3. Rotational Mobility

If a two-spin system is sufficiently rigid (biradicals, triplet molecules, radical pairs formed from complexes), then effects completely analogous to those described above will be observed as a result of rotational mobility[76]. The orientational spin probe method is of particular interest in this instance[78]. Signals due to species where the tensor axis *D* is oriented mainly in one direction can sometimes be isolated with the aid of the magnetophotoselective effect described in Section III or as a result of strong magnetic fields[79]. This makes it possible, in principle, to investigate the kinetics of the rotational disorientation of species with very long correlation times[76]. Measurements performed by this method have also shown that, in vitrified solutions and in polymers, the rotational motions of molecules are polychromatic, i.e. take place with different frequencies in different cages. One of the important problems which investigators have attempted to solve in this manner consists in the choice between two types of elementary motion: rotation in very small random jumps (rotational diffusion) or rotation in large non-correlation jumps. Two different models of elementary processes in the solid phase correspond to these two types of motion: the quasi-crystalline and free-volume models[80]. However, it has not so far been possible to make a final choice (based on experimental data).

4. Conformational Rearrangements

Since the orientation of the reactive groups in molecules is specified by the matrix structure, the study of the dynamics of intra- and inter-molecular rearrangements in the crystal is an essential stage in the investigation of the mechanisms of elementary solid-phase reactions. Fundamentally new possibilities arise in the study of the EPR spectra of radical pairs. In this case the second radical plays the role of a paramagnetic label and a change in the orientation of the radical (or its fragment) leads to a change in the radius-vector of the radical pair r_{eff} and to a marked alteration of the magnetic parameters of the EPR spectrum.

We investigated in detail the structural transformations of iminoxy-radicals in a γ-irradiated 2,4-dinitrophenol matrix at 77 K (Fig. 14),[41,81] and showed that radicals and radical pairs are formed in non-equilibrium conformations with different magneto-relaxation characteristics and thermal stabilities. When the specimens are heated, structural relaxation of two types is observed. In the first, structural transition, there is an appreciable change in the geometry of the CNO fragment due to the difference between the C–N–O angles in the nitrophenol molecule and the iminoxy-radical. The hyperfine interaction constants are also altered and two types of radical pairs are formed with $r_{av} = 4.8$ Å, differing in the orientation of the inter-electron vector in the cell by 5°. On further heating, the radical changes its orientation in the crystal cell slightly, the structure of the fragment being retained. The kinetics of the structural transitions in radicals are consistent with a first-order reaction. The reactive groups are displaced abruptly over small distances (~0.2 Å). The rearrangements give rise to structurally non-equivalent states, which affects the kinetics of the recombination of radicals in the pairs. The kinetics are more complex—the kinetic curve for powders can be fitted by two exponential functions (see Table).

Thus even a small difference in the structure causes a marked alteration of the recombination rate constant. This characteristic is of interest primarily because the occurrence of a large number of intermediate elementary rearrangements can be the reason for the polychromatic kinetics of the recombination reactions. A characteristic feature of the processes investigated is the presence of kinetic isotope effects in the entire chain of transformations, although conformational transitions and recombination involve radicals which do not contain H or D. This demonstrates the major role of the matrix and particularly of hydrogen bonds in the mechanism of radical reactions in 2,4-dinitrophenol. Thus, when the hydroxyl proton is replaced by a deuteron, the rate of the second transition, consisting in the rotation of the molecule as a whole, increases. This may be accounted for by a decrease of the stability of the crystal in parallel with the decrease of the energy of hydrogen bonds when a hydroxyl hydrogen atom is replaced by a deuterium atom in the nitrophenol. The large isotope effect in the recombination reaction (see Table) may be caused by the formation of intermediate complexes of the radicals with the water molecule evolved on radiolysis and captured by the matrix.

The existence of a definite analogy between the conformational relaxation processes considered here and the mechanism of the functioning of complex molecular systems (protein enzymes) is noteworthy[82]. For protein enzymes, it is assumed that, after the formation of a substrate-enzyme complex, rapid relaxation of the active centre

takes place directly and is followed by a slow relaxation of the macromolecule. Presumably the behaviour of the hydrogen-bonded molecules in the nitrophenol crystal is to some extent analogous to that of protein macromolecules. Since a molecular crystal is a significantly simpler system than protein, it is possible to interpret in detail the relaxation transitions in this instance.

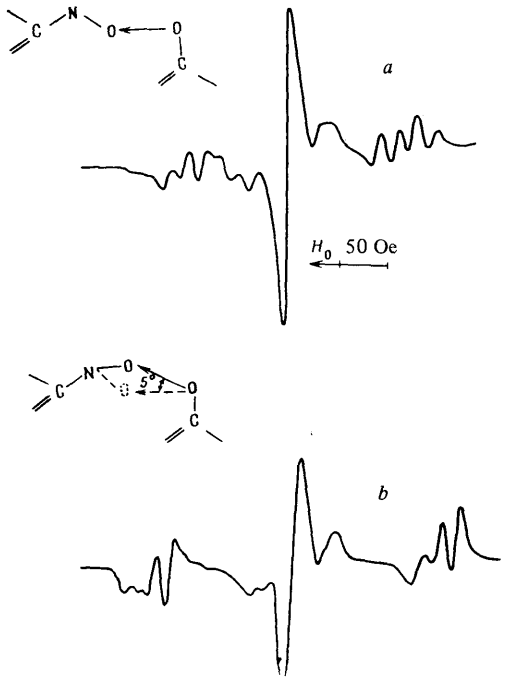
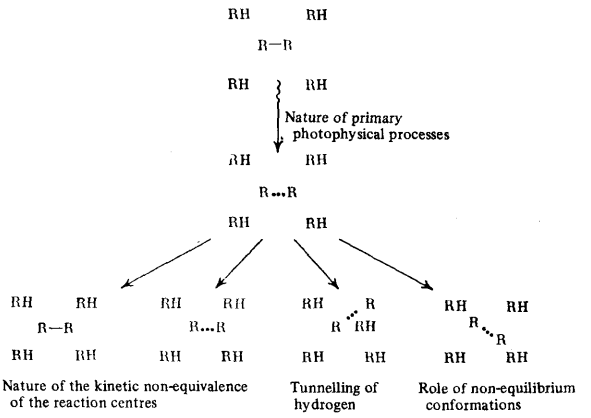


Figure 14. Variation of the EPR spectrum of the "iminoxy-phenoxy"-radical pair in γ-irradiated 2,4-dinitrophenol due to the relaxation of the structure of the CNO fragment. Spectra *a* and *b* were recorded at 77 K and after heating for 10 min at 190 K respectively. Their interpretation is analogous to that illustrated in Fig. 3. In spectra *a* and *b* the C–N–O angle corresponds to the structure of the undamaged molecule and to the equilibrium structure of the iminoxy-radical respectively [81].

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During the decade since the detection of metastable radical pairs, kinetic studies in this field have greatly extended our ideas about the physicochemical foundations of the kinetics of solid-phase reactions. On the basis of the reaction scheme presented at the beginning of Section IV for radical pairs, the most important results of this research can be formulated as follows:



We believe that the demonstration of the kinetic non-equivalence of radicals at the level of the cage, the demonstration of the role of tunnel transitions and conformational changes in solid-phase reactions, and the development of methods for the investigation of the "stereometry of reactions", based on the unique sensitivity of the EPR spectra of radical pairs to changes in the inter-radical vector, are of greatest value. One may hope that further studies in these fields will help to formulate the fundamental characteristics of chemical processes in solid organic substances at least at the level already attained for reactions in the gas phase and dilute solutions.

A completely new field in research on short-lived radical pairs has been initiated recently [83,84]. The results of the latest studies on the structures and spectroscopy of radical pairs, which were not specially considered in this review, may be found in other publications [85–92].

REFERENCES

1. V. V. Voevodskii, "Fizika i Khimiya Elementarnykh Khimicheskikh Protsessov" (The Physics and Chemistry of Elementary Chemical Processes), Izd. Nauka, Moscow, 1969.
2. Y. Kurita, J. Chem. Phys., 41, 3926 (1964).
3. Ya. S. Lebedev. Dokl. Akad. Nauk SSSR, 171, 378 (1966).
4. Ya. S. Lebedev and V. I. Muromtsev, "EPR i Relaksatsiya Stabilizirovannykh Radikalov" (EPR and Relaxation of Stabilised Radicals), Izd. Khimiya, Moscow, 1972.
5. S. Ya. Pshezhetskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii, and V. I. Tupikov, "EPR Svobodnykh Radikalov v Radiatsionnoi Khimii" (The EPR of Free Radicals in Radiation Chemistry), Izd. Khimiya, Moscow, 1972.
6. Ya. S. Lebedev, Symposium, "Svobodno-radikal'nye Sostoyaniya v Khimii" (Free-Radical States in Chemistry), Izd. Nauka, Novosibirsk, 1971, p. 48.
7. B. G. Ershov and A. K. Pikajev, Radiation Research Review, 2, 1 (1969).
8. Y. Kurita, J. Chem. Soc. Japan, 85, 833 (1964).
9. G. M. Zhidomirov and A. L. Buchachenko, Zhur. Strukt. Khim., 8, 111 (1967).

10. J. E. Wertz and J. R. Bolton, "Electron Spin Resonance: Elementary Theory and Practical Applications" (Translated into Russian), Izd. Mir, Moscow, 1975, Chapter 10.
11. G. M. Zhidomirov, Ya. S. Lebedev, S. N. Dobryakov, N. Ya. Shteinshneider, V. L. Gubanov, and A. K. Chirkov, "Interpretatsiya Slozhnykh Spektrov EPR" (Interpretation of Complex EPR Spectra), Izd. Nauka, Moscow, 1975, Chapter 3.
12. M. Iwasaki, K. Toriyama, H. Muto, and K. Nunome, Chem. Phys. Letters, 39, 90 (1976).
13. S. N. Dobryakov, G. G. Lazarev, Ya. S. Lebedev, and M. V. Serdobov, Zhur. Strukt. Khim., 17, 814 (1976).
14. L. P. Bel'kova, O. Ya. Grinberg, A. A. Dubinskii, B. V. Ozherel'ev, and Ya. S. Lebedev, Symposium, "Issledovanie Svobodno-radikal'nykh Sostoyanii v Svyazi s Ikh Rol'yu u Regulyatsii Biologicheskikh Protsessov" (The Study of Free-radicals States in Connection with Their Role in the Regulation of Biological Processes), Pushchino, 1972, Vol. 2, p. 177.
15. O. Ya. Grinberg, A. A. Dubinskii, B. V. Ozherel'ev, A. A. Chistota, and Ya. S. Lebedev, Fiz. Tverd. Tela, 14, 3422 (1972).
16. A. L. Buchachenko, "Khimicheskaya Polyarizatsiya Elektronov i Yader" (Chemical Polarisation of Electrons and Nuclei), Izd. Nauka, Moscow, 1974.
17. T. Cenoud, M. C. Schouler, and M. Decorps, Chem. Phys. Letters, 26, 414 (1974).
18. D. Wiersma, J. H. Lichtenbelt, and J. Kommandeur, J. Chem. Phys., 50, 2794 (1969).
19. I. Itoh, H. Hayashi, and S. Nagakura, Mol. Phys., 17, 561 (1969).
20. W. Flossmann, E. Westhof, and A. Müller, Phys. Rev. Letters, 34, 959 (1975).
21. O. E. Yakimchenko, G. P. Doroshina, and Ya. S. Lebedev, Khim. Vys. Energii, 3, 242 (1969).
22. S. N. Dobryakov, G. G. Lazarev, M. V. Serdobov, and Ya. S. Lebedev, Molec. Phys. (in the Press).
23. S. N. Dobryakov, G. G. Lazarev, Ya. S. Lebedev, and M. V. Serdobov, Zhur. Strukt. Khim. (in the Press).
24. A. V. Zubkov, A. T. Koritskii, and Ya. S. Lebedev, Dokl. Akad. Nauk SSSR, 180, 138 (1968).
25. E. Wasserman and W. A. Yager, J. Phys. Chem., 71, 201 (1967).
26. O. Ya. Grinberg, A. A. Dubinskii, and Ya. S. Lebedev, Dokl. Akad. Nauk SSSR, 193, 848 (1970).
27. G. P. Voskerchyan and Ya. S. Lebedev, Khim. Vys. Energii, 6, 490 (1972).
28. V. I. Barchuk, A. A. Dubinsky, O. Ya. Grinberg, and Ya. S. Lebedev, Chem. Phys. Letters, 34, 476 (1975).
29. V. Zanker and P. Dreyer, Z. angew. Phys., 24, 151 (1968).
30. G. G. Lazarev, Ya. S. Lebedev, and M. V. Serdobov, Izv. Akad. Nauk SSSR, Ser. Khim., 325 (1977).
31. O. Ye. Yakimchenko and Ya. S. Lebedev, Int. J. Rad. Phys. Chem., 3, 17 (1971).
32. M. Iwasaki, T. Jchikawa, and T. Ohnori, J. Chem. Phys., 50, 1984, 1991 (1968).
33. T. Gillbro, P. O. Kinnel, and A. Lund, J. Phys. Chem., 73, 4167 (1969).
34. T. Gillbro and A. Lund, J. Chem. Phys., 61, 1469 (1974).
35. M. Iwasaki, K. Toriyama, H. Muto, and K. Nunome, J. Chem. Phys., 65, 596 (1976).
36. A. A. Dubinskii, O. Ya. Grinberg, A. A. Tabachnik, and Ya. S. Lebedev, Khim. Vys. Energii, 11, 156 (1977).
37. M. Kashiwagi and Y. Kurita, J. Phys. Soc. Japan, 21, 558 (1966).
38. Y. Kurita and M. Kashiwagi, J. Chem. Phys., 44, 1727 (1966).
39. M. Iwasaki and I. Ichikawa, J. Chem. Phys., 47, 4693 (1967).
40. G. Moulton, S. Cernawsky, and D. Straw, J. Chem. Phys., 46, 4292 (1967).
41. O. E. Yakimchenko, N. I. Boguslavskaya, F. I. Dubovitskii, and Ya. S. Lebedev, Khim. Vys. Energii, 10, 373 (1976).
42. N. N. Bubnov, A. I. Prokof'ev, A. A. Volod'kin, I. S. Belostotskaya, and V. V. Ershov, Dokl. Akad. Nauk SSSR, 210, 100 (1973).
43. A. I. Aleksandrov, N. N. Bubnov, G. G. Lazarev, Ya. S. Lebedev, A. I. Prokof'ev, and M. V. Serdobov, Izv. Akad. Nauk SSSR, Ser. Khim., 515 (1976).
44. P. Hess and H. Heusinger, Int. J. Radiat. Phys. Chem., 7, 1 (1975).
45. K. Hamanous, V. Kamartauskas, Y. Tabata, and J. Silverman, J. Chem. Phys., 61, 3439 (1974).
46. T. Gillbro, P. O. Kinnel, and A. Lund, J. Polymer Sci., A-2, 9, 1495 (1971).
47. T. Fujimura and N. Tamura, J. Phys. Chem., 79, 1859 (1975).
48. K. M. Salikhov, A. G. Semenov, and Yu. D. Tsvetkov, "Elektronnoe Spinovoe Ekho i Ego Primenenie" (The Electron Spin Echo and Its Applications), Izd. Nauka, Novosibirsk, 1976, Chapter 6.
49. O. E. Yakimchenko, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1977.
50. O. M. Romanova, Diploma Work, Moscow Physico-technical Institute, Moscow, 1977.
51. A. T. Koritskii, A. V. Zubkov, and Ya. S. Lebedev, Khim. Vys. Energii, 3, 287 (1969).
52. G. G. Lazarev, Ya. S. Lebedev, and M. V. Serdobov, Izd. Akad. Nauk SSSR, Ser. Khim., 2358 (1976).
53. A. B. Jaffe, D. S. Malamant, E. P. Slisz, and J. M. McBride, J. Amer. Chem. Soc., 94, 8515 (1972).
54. P. D. Bartlett and J. M. McBride, Pure Appl. Chem., 15, 89 (1967).
55. R. J. Skinner, R. J. Blaskiewicz, and J. M. McBride, Israel J. Chem., 10, 457 (1972).
56. Z. N. Kulitski, L. M. Terman, V. F. Tsepalov, and V. Ya. Shlyapintokh, Izv. Akad. Nauk SSSR, Ser. Khim., 253 (1963).
57. B. R. Smirnov, G. V. Korolev, and A. A. Berlin, Vysokomol. Soed., 5, 641 (1964).
58. Ya. S. Lebedev and O. Ya. Grinberg, "VIII Mezhdunarodnyi Sympozium po Svobodnym Radikalam, Tezisy Dokladov" (The VIIIth International Symposium on Free Radicals. Abstracts of Reports), Novosibirsk, 1967, p. 206.
59. O. Ya. Grinberg, A. A. Dubinskii, and Ya. S. Lebedev, Kinetika i Kataliz, 8, 660 (1972).
60. O. Ya. Grinberg, A. A. Dubinskii, and Ya. S. Lebedev, Kinetika i Kataliz, 8, 850 (1972).
61. J. M. McBride, J. Amer. Chem. Soc., 93, 6302 (1971).
62. O. E. Yakimchenko, and Ya. S. Lebedev, "Problemy Geterogennogo Kataliza" (Problems of Heterogeneous Catalysis), Izd. Nauka, Moscow, 1973, Vol. XV, p. 212.
63. O. E. Yakimchenko and Ya. S. Lebedev, Khim. Vys. Energii, 5, 271 (1971).
64. A. I. Mikhailov, Ya. S. Lebedev, and N. Ya. Buben, Kinetika i Kataliz, 6, 48 (1965).

65. A. I. Mikhailov, A. I. Bol'shakov, Ya. S. Lebedev, and V. I. Gol'danskii, Fiz. Tverd. Tela, 14, 1172 (1972).
66. V. M. Anisimov and O. N. Karpukhin, Izv. Akad. Nauk SSSR, Ser. Khim., 1914 (1973).
67. V. A. Radtsig, Vysokomol. Soed., 18A, 1899 (1976).
68. V. I. Gol'danskii, Uspekhi Khim., 44, 2121 (1975) [Russ. Chem. Rev., No. 12 (1975)].
69. Ya. S. Lebedev, L. P. Bel'kova, I. S. Gaponova, and O. Ya. Grinberg, Symposium, "Problemy Kinetiki Elementarnykh Khimicheskikh Reaktsii" (Problems of the Kinetics of Elementary Chemical Reactions), Izd. Nauka, Moscow, 1973, p. 80.
70. T. Fujimura and N. Tamura, J. Polymer Sci., B10, 469 (1972).
71. A. L. Buchachenko and A. M. Vasserman, "Stabil'nye Radikaly" (Stable Radicals), Izd. Khimiya, Moscow, 1973.
72. G. I. Likhteishtein, "Metod Spinovykh Metok v Biologii" (The Spin Label Method in Biology), Izd. Khimiya, Moscow, 1974.
73. A. N. Kuznetsov, "Metod Spinovogo Zonda" (The Spin Probe Method), Izd. Nauka, Moscow, 1976.
74. L. P. Bel'kova and Ya. S. Lebedev, Vysokomol. Soed., 17A, 324 (1975).
75. W. Flossmann, A. Müller, and E. Westhof, Mol. Phys., 29, 703 (1975).
76. A. A. Dubinskii, O. Ya. Grinberg, A. A. Tabachnik, and Ya. S. Lebedev, Dokl. Akad. Nauk SSSR, 215, 631 (1974).
77. J. H. Freed, C. V. Bruno, and C. F. Polnaszek, J. Chem. Phys., 55, 5270 (1971).
78. A. A. Dubinskii, V. I. Barchuk, O. Ya. Grinberg, and Ya. S. Lebedev, Fiz. Tverd. Tela, 19, 169 (1977).
79. O. Ya. Grinberg, A. A. Dubinskii, L. G. Oranskii, V. F. Shuvalov, V. I. Kurochkin, and Ya. S. Lebedev, Dokl. Akad. Nauk SSSR, 230, 884 (1976).
80. Ya. S. Lebedev and A. I. Burshtein, Chem. Phys., 12, 259 (1976).
81. O. E. Yakimchenko, O. M. Romanova, and Ya. S. Lebedev, Zhur. Fiz. Khim. (in the Press).
82. L. A. Blyumenfeld, J. Theor. Biol., 58, 269 (1976).
83. E. L. Frankevich and A. I. Pristupa, Pis'ma v Zhur. Eksper. Teor. Fiz., 24, 397 (1976).
84. E. L. Frankevich, A. J. Pristupa, and V. J. Lesin, Chem. Phys. Letters, 47, 304 (1977).
85. N. I. Karsh, E. T. Koh, B. L. Whitsel, and J. M. McBride, J. Amer. Chem. Soc., 97, 6729 (1975).
86. A. P. Kuleshov and V. I. Trofimov, Khim. Vys. Energii, 7, 143 (1973).
87. M. V. Serdobov, A. I. Aleksandrov, and Ya. S. Lebedev, Khim. Vys. Energii, 7, 439 (1973).
88. A. Dulcic and J. N. Herak, Biochim. Biophys. Acta, 319, 109 (1973).
89. D. P. Lin and J. E. Willard, J. Phys. Chem., 78, 2233 (1974).
90. A. B. Jaffe and R. W. Kreilick, Chem. Phys. Letters, 32, 572 (1975).
91. S. H. Glarum and J. H. Marshall, J. Chem. Phys., 62, 956 (1975).
92. F. P. A. Zwegers and C. A. Varma, Chem. Phys., 12, 231 (1976).

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