Russian Chemical Reviews

July 1984

Translated from *Uspekhi Khimii*, 53, 1073-1100 (1984)

U.D.C. 541.124

Kinetics of the Recombination of Radicals and Radical-ions in the Liquid Phase

Kh.S.Bagdasar'yan

The present state of the theory of the recombination of radicals and radical-ions is described on the basis of the diffusion gradient approach and in terms of the approximation of homogeneous chemical kinetics. The experimental data on the cage effect and on the kinetics of the geminate and volume recombination of radicals and radical-ions are discussed within the framework of the methods indicated. Particular attention is devoted to the influence of the viscosity of the medium on these processes. Spin effects in radical and radical-ion pairs and their influence on the recombination kinetics in the absence and presence of an external magnetic field are considered.
The bibliography includes 61 references.

CONTENTS

I. Introduction	623
II. Radical pairs	625
III. Radical-ion pairs	634

I. INTRODUCTION

The recombination of radicals (radical-ions) in the liquid phase is a complex reaction of a special type. The rate of recombination and the composition of the products are determined by the competition between several elementary processes. The complexity of this reaction follows directly from the significant difference between the reactions in the gas and liquid phases. In gases the reaction proceeds on collisions between the molecules; after each collision, the molecules either react or move apart to distances greatly exceeding the molecular diameters, after which collisions take place with other molecules. In the liquid phase chemical reactions proceed on encounters between molecules, which leads to the formation of a "pair" surrounded on all sides by the molecules of the liquid. The pair is characterised by an intrinsic lifetime or a dissociation rate constant. If there is no specific interaction between the molecules of the pair, then its lifetime is determined solely by the molecular movement and is of the order of R^2/D, where R is the sum of the molecular radii and D the sum of the diffusion coefficients. For the usual liquids ($D \cong 2 \times 10^{-5}$ cm^2 s^{-1} and $R \cong 5 \times 10^{-8}$ cm), the lifetime of the pair is $\sim 10^{-10}$ s. In viscous media or in a specific interaction between the molecules of the pair, its lifetime can be much greater.

If a potential barrier of the usual magnitude ($\geq$25 kJ mol^{-1}) exists for the given reaction and there is no specific interaction between the members of the pair, then during the lifetime of the latter the probability of the reaction is very low. In this case the kinetics of the liquid-phase reactions can be considered employing the usual methods of homogeneous chemical kinetics and the concept or pairs becomes superfluous. If there is no potential barrier for the reaction or it is very small, then the rate of such a reaction in the liquid phase can

be represented by the product of the rate of formation of the pairs and the probability of the reaction within the pair. The recombination of radicals (radical-ions) belongs to this class of reactions, which will be the subject of the present review.

Radical pairs are formed not only in the encounters of radicals but they also arise in the primary chemical step. The thermal or photochemical decomposition of molecules into atoms or radicals leads to the formation of a primary or geminate radical pair. Electron transfer from one molecule to another leads to the formation of a geminate radical-ion pair. The photo-ionisation of a molecule with ejection of an electron into the liquid medium results in the formation of a geminate radical-cation–electron pair. The geminate pairs either recombine (geminate recombination) or dissociate with liberation of the two species involved into space. Competition between these processes has come to be called the "cage effect". The radicals released into space react with radical acceptors or solvent molecules, forming secondary radicals. Ultimately all the radicals recombine via the formation of pairs in encounters.

An important characteristic of radical pairs is their spin state. The radical pair undergoes a periodic evolution of its spin state. In the simplest case there is a transition from a purely singlet state (the spins of the unpaired electrons of the radicals pair are antiparallel) to a purely triplet state (the spins of the unpaired electrons are parallel) and conversely via a continuous sequence of mixed states†. A radical pair can recombine only in the singlet state while a radical-ion pair can recombine (reverse electron transfer) also in the triplet state with formation of an electron donor or acceptor molecule in the triplet state. The spin evolution can take place under the influence of an external magnetic field, but is also possible without such a field as a result of the interaction of the unpaired electron with the paramagnetic nuclei of the radical, for example, with protons. The spin evolution and the factors influencing it lead to interesting phenomena such as the chemically induced nuclear polarisation, the influence of the magnetic field on chemical reactions, the magnetic isotope effect, and chemical radioemission. All these phenomena as well as the macroscopic recombination kinetics, the composition of the recombination products, the effectiveness of the initiation of radical chain reactions, and the effectiveness of photochemical systems for the transformation of light (solar) energy are determined by elementary processes involving a radical (radical-ion) pair, i.e. the recombination, dissociation, and spin transformations of the pair.

The difficulty of the theoretical analysis of barrier-free chemical reactions in the liquid phase is associated with the need of a detailed knowledge of the rules governding the molecular movement in liquids and solutions. The simplest version of this approach is the method of molecular pairs (Noyes[1]), according to which the molecules (radicals) of the pair are involved in a series of successive encounters as a consequence of molecular movement. The time between the encounters is defined by a semiempirical formula proposed by Noyes.[1] In each encounter the reaction takes place with a certain probability. The method based on the familiar relation between the disordered character of the molecular movement and diffusion—the macroscopic manifestation of this movement—has come to be widely used. This approach has been called the method of the diffusion gradient or diffusion kinetics. Subsequently we shall make use of the simplest versions of the method of diffusion kinetics. We may also note that the Noyes method has no advantages over the diffusion gradient method, as can be seen from their comparison,[1,2] and futhermore it is inconvenient for the consideration of complex kinetics. In this case the diffusion gradient method can be used in terms of the approximation of chemical kinetics, as will be described in the present review.

II. RADICAL PAIRS

1. Kinetics of the Formation and Dissociation of Radical Pairs

A radical pair is an intermediate short-lived species in radical reactions and its behaviour determines both the kinetics and the chemistry of radical reactions. We shall consider the kinetics of the formation of radical pairs in the encounters of radicals.

In 1918 Smoluchowski[3] considered the kinetics of fast coagulation on the basis of the following model. Small particles are linked to a large particle with a radius R, the size of the former being negligible compared with that of the large particle. The small particles do not interact with one another but disappear following each contact with the large particle. The rate of disappearance (adhesion) of the small particles is determined by the diffusion flux Φ of the small particles to the surface of the large particle:

$$\Phi = 4\pi R^2 D \left| \frac{\mathrm{d}c}{\mathrm{d}x} \right|_R , \qquad (1)$$

where D is the diffusion coefficient of the small particles and $|\mathrm{d}c/\mathrm{d}x|_R$ the concentration gradient of the small particles at the surface of the large particle. The concentration gradient is found by solving the diffusion equation

$$\frac{\partial c}{\partial t} = \frac{D}{x} \frac{\partial^2 (cx)}{\partial x^2} \qquad (2)$$

subject to the initial condition $c(0, x) = c_\infty$ (a uniform distribution of the small particles throughout the entire volume in the initial instant) and the boundary conditions $c(t, R) = 0$ (adhesion following each contact, so that $c = 0$ on the surface of the particle with a radius R) and $c(t, \infty) = c_\infty$ (constant concentration in the region remote from the surface). Expressions for the concentration gradient at the boundary of the large particle,

$$\left| \frac{\mathrm{d}c}{\mathrm{d}x} \right|_R = \frac{c_\infty}{R} [1 + R(\pi D t)^{-1/2}] , \qquad (3)$$

and for the diffusion flux,

$$\Phi = 4\pi R D [1 + R(\pi D t)^{-1/2}] c_\infty , \qquad (4)$$

which determines the rate of adhesion of the small particles to the large particle, follow from the solution of the diffusion equation. It follows from Eqn.(3) that the concentration gradient of the small particles diminishes continuously as those nearest to the surface adhere to it and, after a time of the order of R^2/D, it reaches the constant value c_∞/R. Correspondingly the diffusion flux also reaches a constant value:

$$\Phi = 4\pi R D c_\infty . \qquad (5)$$

In the studies of Vavilov and co-workers,[4] starting from 1928, the diffusion kinetics were first used to describe a molecular process—the quenching of fluorescence. The application of the method of diffusion kinetics to molecular

† The concept of the parallel and antiparallel arrangement of spins in the triplet and singlet states is simplified. Strictly speaking, in the triplet state the electron spins are added together, while in the singlet state they are subtracted.

processes is possible on the basis of the following clear model corresponding to Smoluchowski's theory for the coagulation of colloids.[5] One considers the diffusion of non-interacting point particles in the direction towards a sphere (or away from the sphere) with a radius R (the sum of the molecular radii). The sum of the diffusion coefficients of real molecules is adopted as the diffusion coefficient of the point particles. Depending on the character of the problem, the initial and boundary conditions for the point particles are established. The diffusion flux Φ of the point particles to a sphere with a radius R, subject to the boundary conditions indicated above, is identical with the number of encounters per unit time of real molecules A with a single molecule B and Eqns.(4) and (5) correspond to the non-stationary and stationary cases#. The quantity Φ/c_∞ has the dimensions of a bimolecular rate constant and has been called the "time-dependent rate constant". When a stationary regime is established, this quantity represents the bimolecular rate constant for the formation of pairs. If the two radicals are identical, then the multiplier 1/2 must be introduced into Eqns.(5).

An expression for the rate constant for the dissociation of a contact radical pair can be obtained analogously.[6] For this purpose, it is necessary to solve the diffusion equation subject to the initial condition $c(0, x) = 0$ (at the initial instant the point particles are absent from the given volume) and the boundary condition $c(t, R) = c_0$ (a constant concentration of the point particles is maintained at the boundary of a sphere with a radius R). The solution is

$$k_d = \frac{\Phi}{c_0} = \frac{D}{R^2}\left[1 + R(\pi Dt)^{-1/2}\right], \qquad (6)$$

where Φ is the diffusion flux of the point particles away from the surface of a sphere with a radius R into space.

Up to a time of the order of R^2/D, a constant flux is established with a stationary rate constant for the dissociation of the pairs $k_d = D/R^2$.

Stationary expressions for the rate constant for the formation of pairs ($4\pi RD$) and the rate constant for the dissociation of pairs (D/R^2) lead to the kinetic condition for the diffusion equilibrium:

$$4\pi RD[A][B] = \frac{D}{R^2}[AB]_{eq}. \qquad (7)$$

The equilibrium concentration of pairs $[AB]_{eq}$ is determined by the probability that the molecule B enters a spherical layer with a volume $4\pi R_A^2 R_B$. Assuming that the radii of the molecules A and B are identical, we obtain

$$[AB]_{eq} = 4\pi R^3[A][B], \qquad (8)$$

which agrees with the kinetic Eqn.(7) for the diffusion equilibrium.

2. Kinetics of the Recombination in Space

The kinetics of the recombination of radicals without taking into account explicitly the spin state of the radical pair arising following the encounter of the radicals in space are considered in this Section. The kinetic consequences of the spin state of the radical pair will be considered below.

If the reaction takes place in each encounter of the molecules A and B, then the rate of reaction is equal to the rate of formation of the pairs. Having divided Eqn.(5) by c_∞, we obtain an expression for the bimolecular rate constant at the stationary state:

$$k_{diff} = 4\pi RD. \qquad (9)$$

The Stokes–Einstein formula makes it possible to express RD in terms of T/η, where T is the temperature and η the viscosity of the medium; the ratio T/η is called the fluidity of the medium. If the molecular radii are equal, then

$$RD = \frac{4kT}{6\pi f\eta}, \qquad (10)$$

where k is the Boltzmann constant and f a correction factor of the order of unity§. Having substituted Eqn.(10) in Eqn.(9), we obtain an expression for k_{diff} known in the literature as the Smoluchowski–Debye formula:[7]

$$k_{diff} = \frac{8kT}{3f\eta}. \qquad (11)$$

Eqn.(11) had been derived earlier by Vavilov.[8]

We shall now consider a more general case of diffusion kinetics, where not every encounter of the radicals leads to reaction. In this case the concentration of the point particles on the surface of a sphere with a radius R is not zero but has a finite value, which varies during the reaction, tending to a constant. The solution of the diffusion Eqn.(2) leads in this case to the equation (see, for example, Noyes[1])

$$\Phi = \frac{4\pi RDc_\infty}{1 + 4\pi RD/k_2}\left(1 + \frac{k_2}{4\pi RD}e^{z^2}\operatorname{erfc} z\right), \qquad (12)$$

where k_2 is the bimolecular recombination constant not limited by diffusion (see below) and

$$z = \frac{(Dt)^{1/2}}{R}\left(1 + \frac{k_2}{4\pi RD}\right); \quad \operatorname{erfc} z = \frac{2}{\pi^{1/2}}\int_z^\infty e^{-u^2}du.$$

Different special solutions can be obtained from Eqn.(12). If the rate of reaction is limited by diffusion, i.e. $k_2 \gg 4\pi RD$, then $z \to [(Dt)^{1/2}/R](k_2/4\pi RD) \gg 1$ and $e^{z^2}\operatorname{erfc} z \cong 1/\pi^{1/2}z$ (the first term of the expansion of the expression $e^{z^2}\operatorname{erfc} z$ in series for large values of z). We obtain as a result Eqn.(4). It follows from Eqn.(12) that, after a time greater than R^2/D, a stationary flux and a stationary reaction rate are established. In this case [$t \to \infty$, $z \to \infty$, and the expression in brackets in Eqn.(12) tends to unity], we obtain for the experimental bimolecular rate constant k_{exp} the following expression:

$$k_{exp} = \frac{\Phi}{c_\infty} = \frac{4\pi RDk_2}{k_2 + 4\pi RD}. \qquad (13)$$

This important equation can be obtained immediately by formulating an equation for the diffusion flux Φ of point particles through any spherical surface $4\pi x^2$. This stationary flux is independent of x, i.e. Φ is a constant quantity and is found by solving the following equation:

$$\Phi = 4\pi x^2 D\frac{dc}{dx}. \qquad (14)$$

#In theoretical studies by the diffusion gradient method, the term "probability density" of the observation of molecules at a given site and at a given time is employed. The concentration of point particles is a clear expression of the "probability density".

§For simplicity we shall henceforth use Eqn.(10). If the molecular radii are not equal, then an additional multiplier enters Eqn.(10). For example, if the molecular radii differ by a factor of 2, the multiplier is 1.125; it enters into the correction factor f, which effectively characterises the deviation of the behaviour of real molecules from the Stokes–Einstein formula.

(Boundary conditions:

$$x\to\infty,\ c\to c_\infty;\ x\to R,\ c\to c_0,$$

where c_0 is the stationary concentration of the point particles at the surface of a sphere with a radius R). The integration of Eqn.(14) yields the following expression for the diffusion flux at the boundary of a sphere with a radius R:

$$\Phi = 4\pi RD(c_\infty - c_0) \quad . \tag{15}$$

The flux represents the rate of reaction of all the particles A with a single particle B; consequently $\Phi = k_2 c_0$. Thus it is possible to eliminate c_0 from Eqn.(15) and obtain Eqn.(13).

Two limiting cases follow from Eqn.(13).

1. The diffusion flux limits the rate of reaction, i.e. $4\pi RD \ll k_2$; then $k_{exp} = 4\pi RD = k_{diff}$, which agrees with Eqn.(9). For the usual liquids, k_{diff} is a quantity of the order of 10^{10} litre mol^{-1} s^{-1}.

2. The diffusion flux does not limit the rate of reaction, i.e. $4\pi RD \gg k_2$. Then k_2 is identical with the experimental constant k_{exp}. The constant k_2 is sometimes identified with the bimolecular rate constant for the reaction of the same radicals in the gas phase (see below).

It must be emphasised that, regardless of the reason why not every encounter between the radicals leads to reaction (steric hindrance, spin restrictions, or other causes), the diffusion gradient method leads to Eqn.(13) and all the factors hindering reaction determine the constant k_2. We may also note that Eqn.(9) has a limited range of applicability (see Section 6). However, as a consequence of a certain indefiniteness of the concept of the "sum of radii" and also as a consequence of the application of Eqn.(11) instead of Eqn.(9), it is frequently impossible to decide on the basis of experimental data which equation is valid—Eqn.(13) or (9). If the bimolecular recombination rate constant is measured over a wide range of fluidities of the medium, then Eqn.(13) makes it possible to obtain important information about the elementary processes determining the diffusion recombination kinetics (see below).

The concept of pairs was not used in the derivation of Eqn.(13). The experimental recombination constant k_{exp} can be represented as the product of the rate constant for the formation of pairs and the probability ϕ of reaction in the pair:

$$k_{exp} = 4\pi RD\varphi \quad . \tag{16}$$

One should bear in mind that ϕ is not simply a number less than unity but is a dimensional function of a series of kinetic parameters. It follows from Eqns.(13) and (16) that

$$\varphi = k_2/(k_2 + 4\pi RD).$$

On the other hand, ϕ can be expressed in terms of unimolecular constants for the recombination of the pair (k_1) and its dissociation (k_d). We thus obtain the expression

$$\varphi = k_2/(k_2 + 4\pi RD) = k_1/(k_1 + k_d). \tag{17}$$

The stationary rate constant for the dissociation of the pair is equal to D/R^2, which leads to a relation between the bimolecular constant k_2 and the unimolecular pair recombination constant k_1:

$$k_2 = 4\pi R^3 k_1 \quad . \tag{18}$$

In the general case the constant k_1 has a simpler physical significance than the constant k_2.

3. The "Cage Effect" (Stationary Recombination of Geminate Pairs)

One of the manifestations of the diffusion kinetics of the recombination of radicals is the "cage effect". Frank and Rabinovich[9] observed that the quantum yield of the dissociation of a molecule into atoms or radicals in a liquid medium is smaller than in a gaseous medium. This was explained by the fact that the radicals formed on dissociation are surrounded by solvent molecules which hinders their escape into space and facilitates the reverse reaction. The latter has been called geminate recombination. The proposed explanation has been confirmed by numerous experiments, in particular by the decrease of the quantum yield of the dissociation of molecules with increase of the viscosity of the medium.[1] According to modern terminology, the "cage effect" involves the recombination of geminate pairs in competition with the escape of radicals into space.

The "cage effect" has been studied experimentally by the photolysis or thermolysis in the liquid phase of compounds which readily decompose into radicals (peroxides, azo-compounds, etc.). The reaction is carried out in the presence of effective radical acceptors. The radicals which have escaped into space react with the acceptor to form a product other than the products of the reaction of the radicals in the cage. Thus, in the photolysis of azoethane in n-heptane in the presence of large amounts of styrene, some of the ethyl radicals formed emerge from the cage and add to styrene. In the cage the ethyl radicals either combined to form butane or disproportionate to form ethylene and ethane. The ratio $(C_4H_{10} + C_2H_4)/N_2$ represents the fraction of radicals which have reacted in the cage. This quantity increases from 46 to 84% with decrease of temperature from +99° to −75 °C. The decrease of temperature increases the viscosity of the medium, which hinders the emergence of the radicals from the cage. The photolysis and thermolysis of many compounds in various solvents have been studied at different temperatures and viscosities of the medium; the dimensions of the radicals formed have also been varied.[10,11]

The "cage effect" also determines the effectiveness of initiators of chain radical processes. The effectiveness of the initiators of the polymerisation of vinyl monomers, which determines the fraction of the radicals emerging into space on decomposition of the initiator, has been studied in particular detail. Thus the effectiveness of initiation by azobisisobutyronitrile is 0.5–0.7, while for benzoyl peroxide it amounts to 0.7–1.0.[12]

Numerous experiments have shown that even active radical acceptors, reacting with all the radicals which have emerged into space, cannot compete with the recombination in the cage. The decomposition of azobisisobutyronitrile in liquid bromine may be an exception; in this case products of the recombination in the cage were not detected.[13] It is not clear whether it is possible to reach an unambiguous conclusion from this not altogether usual experiment.

A quantitative theory of the "cage effect" was formulated on the basis of the diffusion gradient method[5] and also the Noyes' method of molecular pairs.[1] Both methods yield identical expressions for the "cage effect" but use different parameters. We shall consider the diffusion gradient method, which makes it possible to formulate the problem exactly. Suppose that the distance between the radicals at the instant of the generation of the pair is l. Under the conditions of the experiments examined above, there is continuous generation and destruction of the radical pairs. As a result of this, after a time of the order of R^2/D (much shorter than the duration of the experiment), a stationary concentration of the pairs is established in the system. According to the

clear model of the diffusion gradient method which we adopted, point particles are continuously generated on the surface of a sphere with a radius l and diffuse "outwards" (dissociation of the pair) and "inwards", where they are destroyed with a certain probability on the inner surface of a sphere with a radius R (geminate recombination). The fraction of the recombination ϕ is determined by the ratio of the diffusion fluxes:

$$\varphi = \frac{4\pi R^2 D \left| \frac{\overleftarrow{\mathrm{d}c}}{\mathrm{d}x} \right|_R}{4\pi l^2 D \left(\left| \frac{\overleftarrow{\mathrm{d}c}}{\mathrm{d}x} \right|_l + \left| \frac{\overrightarrow{\mathrm{d}c}}{\mathrm{d}x} \right|_l \right)} , \qquad (19)$$

where c is the concentration of the point particles and the arrows $\leftarrow$ and $\rightarrow$ indicate the directions of the diffusion fluxes "within" and "outside" a sphere with a radius l. The concentration gradients in Eqn.(19) are found by solving the stationary diffusion equation for the case of spherical symmetry with allowance for the reaction of the radicals with the acceptor¶:

$$\frac{D}{x} \frac{\mathrm{d}^2(cx)}{\mathrm{d}x^2} - k_a c[\mathrm{Ac}] = 0 , \qquad (20)$$

where [Ac] is the acceptor concentration and k_a the rate constant for the reaction of the acceptor with the radicals; the boundary conditions are $x \to \infty$, $c \to 0$; $x = R$, $c = c_0$. The rate of recombination is determined by the diffusion flux through a surface $4\pi R^2$. The rate of recombination can also be represented in the form $k_2 c_0$ (see above). We thus obtain the expression

$$\Phi = 4\pi R^2 D \left| \frac{\mathrm{d}c}{\mathrm{d}x} \right|_R = k_2 c_0 . \qquad (21)$$

This equation makes it possible to eliminate the unknown quantity c_0. As a result, we obtain the following expression for ϕ:

$$\varphi = \frac{R \exp[-b(l-R)]}{l[1 + 4\pi RD(1 + bR)/k_2]} , \qquad (22)$$

where

$$b \equiv (k_a[\mathrm{Ac}]/\mathrm{D})^{1/2} .$$

In the first place it is necessary to estimate bR. The rate constant for the addition of the reactive radical such as the methyl radical or the polymeric vinyl acetate radical to a typical radical acceptor (styrene) at 60 °C is of the order of 10^5 litre mol^{-1} s^{-1} [12] or 0.17×10^{-15} cm^3 s^{-1}. For the usual values $D = 2 \times 10^{-5}$ cm^2 s^{-1} and $R = 5 \times 10^{-8}$ cm and for [Ac] = 10 M, we obtain $k_a[\mathrm{Ac}] = 10^6$ s^{-1} and $bR \leqslant 0.01$. Then Eqn.(22) becomes

$$\varphi = \frac{R}{l} \frac{k_2}{k_2 + 4\pi RD} . \qquad (23)$$

It was found that the quantum yield γ of the photodissociation of iodine decreases with increase of the wavelength of light from 0.83 at $\lambda = 4047$ Å to 0.11 at $\lambda = 7350$ Å.[14] This dependence can be explained by the fact that, with decreased energy of the quantum, the kinetic energy of the translational movement of the iodine atoms moving apart, given by $h\nu - E_{\mathrm{diss}}$, diminishes, which leads to a decrease of l and hence of γ, since $\gamma = 1 - \phi$. This type of dependence has not been observed in he photodissociation of azo-compounds, which leads to the formation of the CH_3 or CF_3 radicals.[15] Evidently in these cases the $h\nu - E_{\mathrm{diss}}$ excess energy is converted into the vibrational energy of the radicals formed and does not lead to their separation, i.e. contact or "almost" contact pairs arise. The results of a study[16] in which it was shown that the "cage effects" are the same in the thermolysis and photolysis of azo-compounds also agree with this conclusion. Since the radicals formed on thermolysis do not possess an excess translational kinetic energy, it is evident that the photolysis also does not lead to the separation of the radicals.

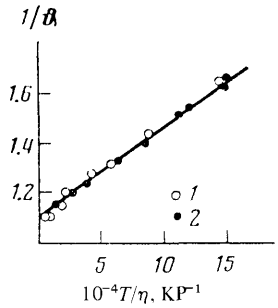


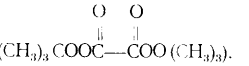
Figure 1. Dependence of $1/\phi$ on T/η; ϕ is the probability of the formation of C_2H_6—the product of geminate recombination in the photodecomposition of azomethane at temperatures from +98° to −72 °C: 1) ethyl acetate; 2) hexane.[5]

If RD is expressed in terms of T/η in accordance with the Stokes–Einstein formula, we obtain from Eqn.(23)

$$\frac{1}{\varphi} = \frac{l}{R} + \frac{l}{R} \frac{8kT}{3k_2 f\eta} . \qquad (24)$$

Figs.1 and 2 present the dependence of $1/\phi$ on T/η according to Eqn.(24) (see also Dobis et al.[15] and Chakravorty et al.[18]). A number of conclusions can be drawn from these data.

1. The ratio $l/R \cong 1$ when the radicals are formed simultaneously with ejection of the N_2 molecule (for example, in the photolysis of CH_3–N=N–CH_3) or $l/R \cong 2$ when the formation of the radicals is accompanied by the ejection of two CO_2 molecules [for example, in the photolysis of



$$(CH_3)_3COOC—COO(CH_3)_3.$$

Evidently a contact radical pair is formed in the former case, which agrees with the considerations expressed above, while in the latter case one CO_2 molecule separates the $(CH_3)_3CO$ radicals at the instant of formation of the pair, so that $l/R \cong 2$.

2. The slope of the linear $1/\phi$–T/η plots makes it possible to calculate the quantity $k_2 f$. This feature requires a more detailed discussion. The geminate recombination of the $\dot{C}H_3$ and $\dot{C}F_3$ radical depends little on the nature of the solvent and ϕ is determined solely by the quantity T/η, while the recombination of t-butoxy-radicals exhibits a definite dependence on the solvent.[17] The straight line in Fig.2 corresponds to aliphatic solvents. For olefins and aromatic solvents with the same fluidities of the medium, the quantities $1/\phi$ are much greater, which indicates smaller values of the

¶ In Denisov's review,[10] this method of analysis of the "cage effect" has been erroneously called the method of "one-dimensional translational diffusion".

constant k_2. For alcohols, the values of k_2 are even smaller, since only traces of geminate recombination products have been detected in such media. The deviation from the straight line must be explained by the specific interaction of the butoxy-radicals with the solvents indicated, which hinders the recombination and facilitates the emergence of the radical into space.[17]

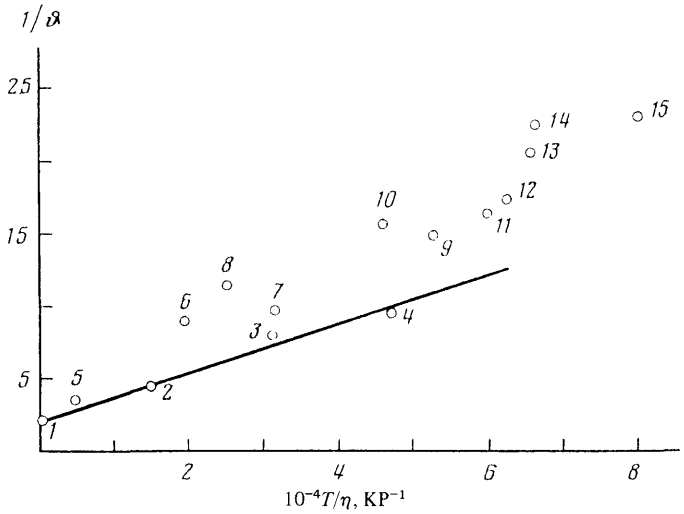


Figure 2. Dependence of $1/\phi$ on T/η; ϕ is the probability of the geminate recombination of t-butoxy radicals in various media: 1) liquid paraffin; 2) hexadecane; 3) dodecane; 4) decane; 5) dimethyl phthalate; 6) tetralin; 7) *o*-dichlorobenzene; 8) acetophenone; 9) cumene; 10) α-methylstyrene; 11) ethylbenzene; 12) cyclohexane; 13) toluene; 14) benzene; 15) oct-1-ene. The plot has been constructed on the basis of the data of Niki and Kamiya.[17]

Table 1. Kinetic constants for the recombination of radicals.

Constant, litre mol^{-1}s^{-1}	$\dot{C}H_3 + \dot{C}H_3$	$\dot{C}F_3 + \dot{C}F_3$	$(CH_3)_3\dot{C}O + O\dot{C}(CH_3)_3$
$10^{-10}\,k_2$	6.0 [5]; 11.7 [15]	1.4 [18]	0.41 [17]
$10^{-10}\,k_{gas}$	2.0 [19]	2.3 [19]	0.13±0.05 [20]
$10^{-10}\,Z^{gas}$	8.2	6.8	6.6

The constants k_2, determined from the slopes of the plots of $1/\phi$ against T/η (the multiplier f was assumed to be 0.65), are compared in Table 1 with the experimental recombination constants for the same radicals in the gas phase k_{gas} and with the calculated number of collisions Z in gases. The recombination constants in the gas phase for the methyl and trifluoromethyl radicals are ~1/4 of the number of collisions. This ratio corresponds to the probability that the spins of the colliding radicals are antiparallel. The recombination constant for the butoxy-radicals in the gas phase is much smaller than the number of collisions. For the methyl and butoxy-radicals, the rate constant k_2 is greater by a factor of 3–4 than the recombination constant in the gas phase. This can be explained by the fact that the geminate pair of radicals formed on photolysis is in a singlet state.[5] A difference between the constants has not been observed for the trifluoromethyl radical. However, one should treat all these conclusions with caution bearing in mind the experimental accuracy. There is only one reliable conclusion: the constants k_2 differ from the recombination constants in gases k_{gas} by a factor not greater than 2–3.

If a contact radical pair is formed, i.e. $R = l$, then the probability of recombination can be represented by Eqn.(17):

$$\varphi = k_1/(k_1 + k_d). \qquad (17)$$

Since the lifetime of the radical pair formed on photolysis or thermolysis is of the order of R^2/D, presumably a nonstationary value corresponding to Eqn.(6) must be adopted for k_d. If, however, the duration of the photolysis (thermolysis) greatly exceeds the lifetime of the pair, then a stationary value of D/R^2 enters into Eqn.(17). This can be demonstrated by the following calculation. Suppose that the pairs are formed at a rate I, whereupon $I\mathrm{d}\tau$ pairs are formed during the period $\mathrm{d}\tau$. The number of recombined pairs $\Delta(RR)$ during time t is defined by the expression

$$\Delta(RR) = k_1 I \int_0^t \left\{k_1 + \frac{D}{R^2}\left[1 + \left(\frac{R^2}{\pi D\,(t-\tau)}\right)^{1/2}\right]\right\}^{-1} \mathrm{d}\tau\,, \qquad (25)$$

After integration, it can be shown that, for $t \gg R^2/D$, the fraction of the recombined pairs is given by the expression

$$\varphi = \frac{\Delta(RR)}{It} = \frac{k_1}{k_1 + D/R^2}\,. \qquad (26)$$

In pulsed laser photolysis, where $t_{pulse} \cong R^2/D$, a nonstationary expression must be used for k_d (see below).

If the existence of very effective radical acceptors, for which $k_a[\mathrm{Ac}] > 10^6\ \mathrm{s}^{-1}$ is assumed, then there is a possibility of competition between the acceptors and geminate recombination. Having put $l = R$, Eqn.(22) can be expressed in the form

$$\varphi = \frac{\varphi_0}{1 + (1-\varphi_0)\,(k_a[\mathrm{Ac}]R^2/D)^{1/2}} \simeq \varphi_0\{1 - (1-\varphi_0)(k_a[\mathrm{Ac}]R^2/D)^{1/2}\}\,, \qquad (27)$$

where

$$\varphi_0 = k_2/(k_2 + 4\pi RD) = k_1/(k_1 + D/R^2)$$

is the fraction of geminate recombination in the absence of radical acceptors. It follows from Eqn.(27) that, in the presence of effective acceptors, ϕ should diminish as a linear function of $[\mathrm{Ac}]^{1/2}$. The influence of acceptors on recombination in the cage has also been represented in other forms,[1,21] but the linear dependence of ϕ on $[\mathrm{Ac}]^{1/2}$ remains.

4. Kinetics of the Recombination of Geminate Radical Pairs

The kinetics of geminate recombination can be investigated only by pulse methods. In the first study of this type,[22] the dissociation of the iodine molecule into atoms and their subsequent recombination in hexadecane and in carbon tetrachloride were followed by the method of picosecond photolysis. After 300–500 ps, geminate recombination reaches completion and an appreciable fraction of the iodine atoms emerge into space. An analogous study has been carried out in liquid xenon.[23] The kinetics of the geminate recombination in these studies have been discussed on the basis of the Noyes method of molecular pairs.[1] In this procedure use is made of the function $h(t)$, which expresses the probability that, after the first encounter between the molecules (radicals), a

second encounter takes place at a time between t and $t + dt$. Noyes proposed an approximate expression for the function $h(t)$:

$$[h(t) = pt^{-3/2}e^{-qt}] \quad , \qquad (28)$$

where p and q are constants. In this case the first encounter involves the formation of the geminate pair and the second encounter leads to reaction with a certain degree of probability. [The exact expression for the function $h(t)$ obtained by the diffusion gradient method[2] differs greatly from Eqn.(28).] Only an approximate agreement between Eqn.(28) and experiment has been noted.[22] In another study the[23] agreement with experiment was achieved by selecting three parameters. There is reason to believe that the picosecond dissociation of I_2 is complicated by phenomena which have no bearing on the geminate recombination.[24]

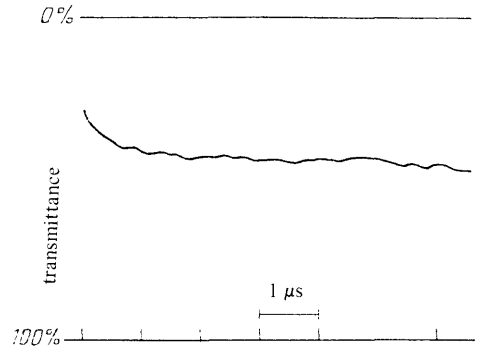


Figure 3. Kinetics of the geminate recombination of indandionyl radicals in liquid paraffin at 0 °C; T/η = 40 K P^{-1}.[26] For explanation, see text.

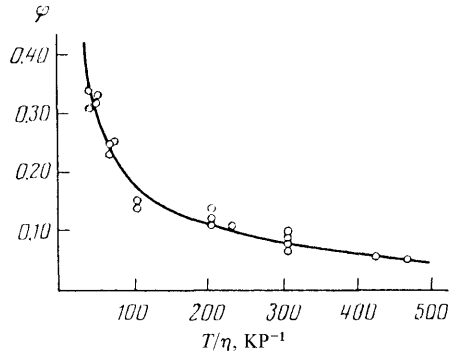
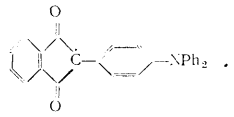


Figure 4. The fraction of the geminate recombination ϕ of indandionyl radicals as a function of the fluidity of the medium.[25]

The kinetics of the geminate recombination of indandionyl radicals, arising in the nanosecond photolysis of the corresponding dimer, have been studied:[25,26]



The geminate recombination has been observed only in viscous media (mixtures of hexane with liquid paraffin) in the region of fluidities below 500 K P^{-1}. Fig.3 illustrates typical kinetics of geminate recombination. The initial passage of the probing beam is determined by radical pairs and the plateau is due to the radicals which have escaped into space. Fig.4 shows the dependence of the fraction of geminate recombination ϕ on T/η. Analysis of the data on the "cage effect" leads to the conclusion that contact (or "almost" contact) radical pairs are formed on photolysis and thermolysis even in a mobile medium. Only on photodissociation of I_2 do I atoms move apart to distances exceeding the sum of their radii.[14]

We shall consider the kinetics of the geminate recombination of the contact radical pairs in terms of the "approximation of chemical kinetics".[6,26,27] The essential feature of this approximation consists in the fact that the rate of destruction of the given species is formulated in terms of the kinetic equations of homogeneous chemical kinetics, i.e. as the sum of the rates of formation and destruction of the given species via different pathways, including both chemical and diffusion processes. The rate constant for diffusion process, which in the general case depend on time, is found by solving the corresponding diffusion equation for point particles. For example, the rate constants for the formation and dissociation of pairs are determined by Eqns.(4) and (6). In terms of this approximation, the destruction of the contact radical pairs, which have arisen after the completion of the pulse, is determined by the equation

$$-\frac{dn}{dt} = k_1 n + \frac{D}{R^2}[1 + R(\pi D t)^{-1/2}]n \, . \qquad (29)$$

The first term represents the destruction of the pairs as a result of geminate recombination and the second as a result of the dissociation of the pairs [see Eqn.(6)]. The integration of Eqn.(29) yields

$$\frac{n}{n_0} = \exp\{-[(1 + a^2)k_1 t + 2a(\pi k_1 t)^{1/2}]\} \, , \qquad (30)$$

where $a^2 = D/R^2 k_1$ is the ratio of the stationary rate constant for the dissociation of the pair to the geminate recombination constant and n_0 is the initial concentration of the pairs. The fraction of pairs which have recombined during time t is

$$\varphi(t) = k_1 \int_0^t \frac{n}{n_0} dt = [1 - \exp(A^2 - z^2) - \sqrt{\pi} A \, e^{A^2}(\mathrm{erf}\, z - \mathrm{erf}\, A)]/(1 + a^2), \qquad (31)$$

where

$$A = a/[\pi(1 + a^2)]^{1/2} \text{ and } z = A + [(1 + a^2)k_1 t]^{1/2}.$$

When $t \to \infty$, Eqn.(31) becomes

$$\varphi = [1 - \sqrt{\pi} A \, e^{A^2} \mathrm{erfc}\, A]/(1 + a^2) \, . \qquad (32)$$

Eqn.(32) represents the fraction of recombined radical pairs under the conditions of non-stationary recombination kinetics. In terms of the approximation of chemical kinetics, this quantity is smaller than the fraction of the recombined radical pairs under stationary conditions, which is $(1 + a^2)^{-1}$.

5. The Multiplicity of the Radical Pair

For a more rigorous description of the kinetics of the recombination of a radical pair, it is necessary to take account of its multiplicity. The radical pair can exist in two extreme states: singlet or triplet. It follows from the quantum theory that the multiplicity of the pair varies continuously through a sequence of mixed states (see, for example, Buchachenko[28]). This phenomenon has come to be called spin evolution. The probability of the recombination of the radical pair is higher the greater the contribution of the singlet state to the multiplicity of the pair. The radical pair existing in a purely triplet state cannot recombine.

There are various mechanisms of the changes in the multiplicity of the radical pair. The following are of real importance.

1. The Δg-mechanism. This mechanism is manifested following the imposition of an external magnetic field. According to this mechanism, the rate of spin evolution is determined by the difference between the magnetic energies of the unpaired electrons of the radical pair. The energy of an electron in a magnetic field H is $\frac{1}{2}g\beta H$, where β is the Bohr magneton (0.927×10^{-20} erg G^{-1}) and g a proportionality coefficient—the so-called g-factor, which is determined from the EPR spectrum. For a free electron, $g = 2.0023$; for the unpaired electron in the radical, the g-factor differs from this value as a consequence of the spin–orbital coupling and depends on the type of the radical. In a magnetic field the triplet state of the radical pair is split into three sublevels T_-, T_0, and T_+, among which only the energy of the T_0 sublevel coincides with that of the pair in a singlet state (subject to the condition that there is no exchange interaction in the pair). Only T_0–S transitions, whose probability vary with time as $\sin^2(\frac{1}{2}\Delta g\beta Ht/h)$,[29] where $h = h/2\pi$ (h is the Planck constant), therefore occur in a magnetic field. In this expression

$$\left(\frac{1}{2}\right)\Delta g\beta H/\hbar = \left(\frac{1}{2}\right)2\pi\Delta g\beta H/h$$

represents the difference between the magnetic energies of the unpaired electrons expressed in units of rad s^{-1}. [This unit of measurement of the energy is obtained by dividing the magnetic energy of the electron $\frac{1}{2}g\beta H$ (ergs) by h (erg s), which yields the energy in s^{-1}, and by multiplying by 2π, which yields the energy in units of rad s^{-1}.]

If in the initial instant the pair exists in a purely singlet state, then after a time t_S, whereupon $\frac{1}{2}2\pi\Delta g\beta Ht_S/h = \pi/2$, the pair passes to a purely triplet state. The quantity $k_S = 1/t_S$ can be adopted, with some approximation, as the constant of the T_0–S transition, i.e. $k_S = 2\Delta g\beta H/h$. Since the quantities Δg are usually in the range 10^{-2}–10^{-3}, it follows that we obtain $k_S = 2.8 \times 10^8$–2.8×10^7 s^{-1} for $H = 10^4$ G.

2. The HFI-mechanism. Another mechanism leading to spin evolution is a consequence of the magnetic interaction of the unpaired electron with paramagnetic nuclei (usually with protons, but also with ^{13}C, ^{17}O, ^{19}F, ^{31}P, etc. nuclei). Since this interaction leads to splitting of the EPR line into a series of components, i.e. to a hyperfine structure of the spectrum, it has come to be called the hyperfine interaction (HFI). Quantitatively the HFI interaction is characterised by an HFI constant, which is determined from the EPR spectrum and is usually expressed in gauss. The HFI-mechanism of spin evolution also depends on the external magnetic field, but this dependence is of a type different from that in the case of the Δg-mechanism. In the absence of the magnetic field, all three sublevels of the triplet state of the pair are degenerate and their energies coincide with the energy of the singlet state. Under these conditions, the transition from the singlet state is to all three sublevels of the triplet state. When an external magnetic field is imposed, only the T_0–S transition takes place as a consequence of the splitting of the triplet level, which usually leads to a decrease of the probability of the transition. We may note that the necessary splitting of the triplet level is achieved in magnetic fields amounting to several tens or hundreds of gauss.

A quantitative analysis of the HFI-mechanism is difficult, particularly because the radical pair usually contains several paramagnetic nuclei, for example, protons, which are in the general case characterised by different HFI constants and this leads to a complex picture of spin evolution. Expressions have been published[29] for the probabilities of the S–T transitions for certain simple model radical pairs. For example, for the radical pair

$$\dot{R}^1 \cdots \dot{R}^2 \begin{matrix} \nearrow H \\ \searrow H \end{matrix}$$

in the absence of an external field, the probability of the S–T transition varies with time as $^2/_3 \sin^2(^3/_4At)$. The parameter A (rad s^{-1}) is related to the HFI energy, equal to $a\beta$, by the expression $A = 2\pi a\beta/h$, where a is the HFI constant (G) and β the Bohr magneton (erg G^{-1}). As in the case of the Δg-mechanism, for the time t_S corresponding to a change in the multiplicity of the pair we shall adopt the condition $^3/_4At_S = \pi/2$, whence it follows that $1/t_S = k_S = 3a\beta/h$. If $a = 100$ G, then $k_S = 0.4 \times 10^9$ s^{-1}. For other radical pairs, one should expect values of k_S of the same order of magnitude for the same values of a. If one radical contains m protons and the other n protons, then the extent of the HFI in the pair can be approximately calculated with a single effective HFI constant a_{eff}, which is defined by the formula

$$a_{\text{eff}} = \left(\sum_m a_m^2 + \sum_n a_n^2\right)^{1/2} . \qquad (33)$$

The periodic evolution of the spin state of the pair was observed experimentally for the first time by Anisimov et al.[30] A solution of tetramethylethylene (D) and perdeutero-p-terphenyl (A) in a non-polar solvent proved to be a convenient object for investigation. The ionisation of the solvent under the influence of ^{90}Sr radiation generates pairs of radical-ions ($D^+.A^-$) as a result of electron capture by the molecule of A and electron transfer from D to the solvent radical-cation. In the radical-ion D^+ all the protons are equivalent, while the HFI constants for A^- are small. In this case the picture of spin evolution simplifies and can be observed from the periodic maxima of the recombination fluorescence arising on recombination of the pair (electron transfer from A^- to D^+) with formation of a fluorescent molecule A*. These maxima are observed particularly clearly following the imposition of a magnetic field (3300 G), which leads to a further simplification of the picture of spin evolution as a consequence of the "disconnection" of the T_+ and T_- states. The recombination fluorescence maxima continued in succession over a period of 22 ns, which corresponded, according to a theoretical calculation,[31] to the maximum in the contribution of the singlet state of the pair.

An important feature of the HFI-mechanism is that a change in the multiplicity of the radical pair is accompanied by selection with respect to the orientations or reorientations of the spins of the paramagnetic nuclei. Since the relaxation of the nuclear spins is slow (minutes), the ratio of the molecules with the orientation of the nuclear spin along the magnetic field and in opposition to the field in the radical pair recombination products differs from the Boltzmann ratio. This phenomenon, which has come to be called chemically induced nuclear polarisation, has been described in detail in

a monograph[28] and in a review.[32] The phenomenon of chemically induced radioemission is also associated with the polarisation of nuclear spins on recombination of radical pairs.[33] If the radical pair contains a paramagnetic isotope, for example ^{13}C, then, as a consequence of the influence of the paramagnetic nucleus on the spin evolution, certain recombination products are enriched in the paramagnetic isotope—the magnetic isotope effect.[32,34,35] For all these phenomena, the observed effect is determined by competing processes involving spin evolution, recombination, and diffusion separation of the pair. The discussion of these interesting phenomena is outside the framework of the present review.

It is also necessary to consider the influence of the exchange interaction of unpaired electrons on the spin evolution. If this interaction is intense, then the spin evolution is hindered as a consequence of the appearance of an energy difference between the T_0 and S states. It is usually assumed, following the Noyes theory, that the radicals of the pair execute a series of repeating encounters as a consequence of molecular movement. In the intervals between these encounters the exchange energy is small and spin evolution reaches completion. However, spin evolution can be completed also in contact (or "almost" contact) pairs. As a result of the diffusional rotation of the radicals of the pair, the wave functions of the unpaired electrons do not overlap for a considerable proportion of the lifetime of the pair and the exchange interaction is therefore weak. The characteristic time of rotational diffusion is of the same order of magnitude as the characteristic time of translational diffusion[36] and spin evolution can therefore compete with the diffusional separation in the pair and also with the recombination of the radicals of the pair.

6. The Probability of the Recombination of the Radical Pair taking into account Spin Evolution

Theoretical consideration of the recombination of radical pairs taking into account spin evolution and the influence of the magnetic field is a complex task. It was shown in the previous Section that spin evolution can be approximately characterised as unimolecular $T-S$ transitions. In terms of the approximation of the methods of chemical kinetics, the behaviour of the radical pairs can then be described by the following scheme of elementary processes,[26] different variants of which have been used in many experimental studies:

$$\begin{array}{ccc} R{-}R & \underset{k_1}{\overset{}{\leftarrow}} & {}^1(R\cdot R) \underset{k_S}{\overset{3k_S}{\rightleftarrows}} {}^3(R\cdot R) \\ & & \downarrow k_d \qquad \downarrow k_d \\ & & R+R \qquad R+R \end{array} .$$

We shall carry out a kinetic analysis of this scheme.[26] The rate constant for the transition from the triplet to the singlet state is designated by k_S, whereupon the rate constant for the reverse transition (in the absence of a magnetic field) is $3k_S$ as a consequence of the triple degeneracy of the triplet state of the pair. Suppose that at a certain instant there are [P] pairs, among which there are [S] singlet pairs and [T] triplet pairs. The fraction of pairs which have recombined during time t is

$$\varphi(t) = \frac{k_1}{[P]} \int_0^t [S]\,dt \quad . \tag{34}$$

The concentration of the singlet pairs can be found in terms of the approximation of chemical kientics by solving a system of kinetic equations for the singlet and triplet pairs:

$$\frac{d[S]}{dt} = k_S[T] - k_1[S] - k_d[S] - 3k_S[S] \; ; \tag{35}$$

$$\frac{d[T]}{dt} = -k_S[T] - k_d[T] + 3k_S[S] \; . \tag{36}$$

In the general case the constant k_d depends on time in accordance with Eqn.(6). We shall consider the application of Eqns.(34)–(36) in the description of geminate and volume recombination.

Geminate recombination. Geminate pairs arise either in the singlet or triplet state depending on the spin state of the initial molecule at the instant of dissociation. In the general case the characteristic time of geminate recombination is of the same order of magnitude as the lifetime of the pair. Consequently the following non-stationary quantity must be adopted for k_d:

$$k_d = \frac{D}{R^2}[1 + R(\pi D t)^{-1/2}] \; .$$

We shall consider special cases.

(a) The pairs arise in the triplet state and the time of transition to the singlet state is much greater than the dissociation time of the pair, i.e. $k_d \gg k_S$. In this case geminate recombination does not occur and all the pairs dissociate.

(b) The pairs arise in the triplet state, the transition to the singlet state is slow, and the recombination in the singlet state is rapid, i.e. $k_1 \gg k_S$. The rate of recombination is then determined by the rate of the process $T \to S$, which is equal to $k_S[T]$. Since in this case $[T] \gg [S]$, then neglecting the term $3k_S[S]$ in Eqn.(36), we arrive at Eqns.(29) and (32), in which k_S replaces k_1, i.e. the probability of the recombination is determined by the rate of transition of the pair to the singlet state in competition with the diffusional separation of the pair.

(c) The pairs arise in the singlet state and the transition to the triplet state is slow, i.e. $k_d \gg k_S$. The first two terms of Eqn.(35) can then be rejected, leading to Eqns.(29) and (32). In this case the probability of recombination is independent of the rate of spin evolution.

(d) If the spin evolution is very rapid, i.e. $k_S \gg k_d$ and $k_S \gg k_1$, then, regardless of the initial spin state of the pair, a spin equilibrium is established in which $[T] = 3[S]$. Having added together Eqns.(35) and (36), we again arrive at Eqn.(29), in which $k_1/4$ replaces k_1. This special case obtains in a viscous medium at a very high rate of spin evolution.

Thus, for all the special cases considered, the kinetics of the geminate recombination are described by Eqn.(29) and we obtain Eqn.(32) for the probability of recombination, in which the constant k_1 is modified for different special cases, as shown above.

In order to obtain a general expression for the kinetics of geminate recombination, it is necessary to solve Eqns.(35) and (36). An approximate solution can be obtained if the average value of k_d during the lifetime of the pair τ is adopted:

$$\bar{k}_d = \frac{D}{R^2\tau} \int_0^\tau [1 + R(\pi D t)^{-1/2}]\,dt \simeq 2.13D/R^2 \; . \tag{37}$$

The coefficient 2.13 is obtained if one puts $\tau = R^2/D$. We then obtain for the probability of geminate recombination the same equations as for the volume recombination (see below), in which the average value $\bar{k}_d$ should be substituted for k_d.

Volume recombination. The geminate pairs which have dissociated with liberation of the radicals into space give rise to a volume concentration of radicals. The recombination takes place in space following the encounter of the radicals which have emerged from different pairs and produced secondary

pairs. Since the characteristic time of the volume recombination greatly exceeds the lifetime of the pair and the time of attainment of the stationary value of k_d, it follows that $k_d = D/R^2$ (see above). In this case Eqns.(35) and (36) are easily solved under specified initial conditions and expressions are obtained for [S] and [T] as functions of time. Integration of Eqn.(34) from 0 to ∞ yield expressions for ϕ for pairs arising in the singlet state:

$$\varphi_S = \frac{k_S k_1 + k_d k_1}{k_S k_1 + 4k_S k_d + k_1 k_d + k_d^2} \quad (38)$$

and for those arising in the triplet state:

$$\varphi_T = \frac{k_S k_1}{k_S k_1 + 4k_S k_d + k_1 k_d + k_d^2} \quad . \quad (39)$$

Since one-quarter of the pairs are formed in the singlet state and three-quarters are formed in the triplet state in an encounter between radicals in space, the overall probability of the recombination is defined by the expression

$$\varphi = \frac{1}{4}\varphi_S + \frac{3}{4}\varphi_T \quad (40)$$

or

$$\varphi = \frac{k_S k_1 + \frac{1}{4} k_1 k_d}{k_S k_1 + 4k_S k_d + k_1 k_d + k_d^2} \quad . \quad (41)$$

Certain special cases are of interest.

1. During the lifetime of the pair there is insufficient time for spin evolution, i.e. $k_d \gg k_S$. It then follows from Eqn.(41) that

$$\varphi = \frac{1}{4} k_1/(k_1 + k_d) \quad . \quad (42)$$

If in addition we have under these conditions $k_1 \gg k_d$, then $\phi = {}^1/_4$. In this case the bimolecular recombination constant $k_{exp} = 4\pi RD/4$. This case can obtain in a fluid medium and also for a low rate of spin evolution.

2. The spin transformation times are much shorter than the lifetime of the pair, i.e. $k_S \gg k_d$. We then have

$$\varphi = k_1/(k_1 + 4k_d). \quad (43)$$

If in addition $k_1 \gg k_d$, then $\phi = 1$ and $k_{exp} = 4\pi RD = k_{diff}$. This case can obtain in viscous media and for high rates of spin evolution.

It is seen from the above analysis that the expressions for the radical recombination rate constant in the form $k_{exp} = 4\pi RD/4$ or $k_{exp} = 4\pi RD$, which are frequently encountered in the literature, in reality obtain only in special cases, while Eqn.(41) and special cases of the latter [Eqns.(42) and (43)] correspond to more realistic conditions and constitute a generalisation of Eqn.(17) obtained without taking into account spin transformations.

7. Determination of the Kinetic Constants for Radical Pairs from Experimental Data

A method has been proposed[26] for the determination of the kinetic constants k_1 and k_S from experimental data for the kinetics of the volume and geminate recombination over a wide range of fluidities of the medium T/η.

Volume recombination. The probability of the recombination of the pair ϕ_{exp}, formed in an encounter between radicals, can be determined experimentally from the equality

$$\varphi_{exp} = \frac{k_{exp}}{4\pi RD} \quad , \quad (44)$$

where k_{exp} is the bimolecular recombination constant. Having expressed RD in terms of T/η by means of the Stokes–Einstein formula [Eqn.(10)], we obtain

$$\varphi_{exp} = \frac{3k_{exp} f\eta}{8kT} \quad . \quad (45)$$

We set ϕ_{exp} equal to the theoretical quantity ϕ (see above). It is then possible to determine from the experimental data the constants k_1 and k_S; for this purpose, it is necessary to measure k_{exp} over a wide range of fluidities of the medium. We shall explain the method for the determination of the kinetic constants in relation to the recombination of indandionyl radicals arising in the nanosecond photolysis of the corresponding dimer.[26] In the above study the bimolecular recombination constant k_{exp} was measured in mixtures of toluene and liquid paraffin over a wide range of fluidities of the medium—from 50500 to 41 K P^{-1}. In the region of low fluidities ϕ_{exp} reaches a constant value, which is evidently unity. It follows from this normalisation that $f = 0.65$. With increase of the fluidity of the medium to 500 K P^{-1}, all the singlet pairs recombine with a probability of unity; the rate of recombination of triplet pairs is determined by the rate of their conversion into singlet pairs in competition with the dissociation of the pair. Consequently in this range of fluidities we have $k_1 \gg k_S$ and $k_1 \gg k_d$. It then follows from Eqns.(39) and (40) that

$$\varphi_{exp} = \frac{1}{4} + \frac{3}{4}\frac{k_S}{k_S + k_d} \quad , \quad (46)$$

where $k_d = D/R^2$. Application of the Stokes–Einstein formula leads to the expression

$$(1 - \varphi_{exp})/(\varphi_{exp} - 0.25) = \frac{4kT}{6\pi f\eta R^3 k_S} \quad . \quad (47)$$

A plot of $(1 - \phi_{exp})/(\phi_{exp} - 0.25)$ against T/η is presented in Fig.5. $R^3 k_S = 0.3 \times 10^{-13}$ cm^3 s^{-1} can be obtained from the slope of the straight line†. For a fluidity of the medium in excess of 3000 K P^{-1}, the experimental points deviate from the straight line. Consequently in this range of values of T/η not all the singlet pairs recombine and some of them dissociate.

In the region of high fluidities of the medium, it has been found that $\phi_{exp} < 0.25$. Evidently under these conditions not only all the triplet pairs but also some of the singlet pairs dissociate. Consequently $\phi_T = 0$ and $k_d \gg k_S$ for the singlet pairs, while k_1 and k_d are of the same order of magnitude. For this range of values of T/η, it follows from Eqns.(38) and (40) that

$$\varphi_{exp} = \frac{1}{4} k_1/(k_1 + k_d) \quad . \quad (48)$$

Having set Eqns.(45) and (48) equal to each other, we obtain

$$\frac{1}{k_{exp}} = \frac{3f\eta}{2kT} + \frac{1}{\pi R^3 k_1} \quad . \quad (49)$$

Fig.6 illustrates the dependence of $1/k_{exp}$ on η/T in the region of high fluidities and it follows from the plot that $f = 0.33$ and $R^3 k_1 = 9.1 \times 10^{-13}$ cm^3 s^{-1}. The absolute values of the constant k_1 and k_S can be determined if reasonable

---

†The quantity $\bar{k}_d = 2.13\, D/R^2$ has been used.[26] As shown above, $k_d = D/R^2$ should be employed for the volume recombination. The constants k_1 and k_S quoted by Bagdasar'yan and co-workers[26,37] should be reduced by a factor of 2.13.

values are assumed for R. The study of the kinetics of the geminate recombination makes it possible to determine R directly from the experimental data (see below). Thus the following values of the constants have been obtained:

$$R=14.5 \text{ Å}, \ k_1=2.7\cdot10^8 \text{ s}^{-1}, \ k_S=9.0\cdot10^6 \text{ s}^{-1}.$$

For these values of the kinetic constants, Table 2 lists the recombination probabilities for singlet and triplet pairs calculated by Eqns.(38) and (39) and also the overall probability of recombination in the encounters between radicals in accordance with Eqn.(40).

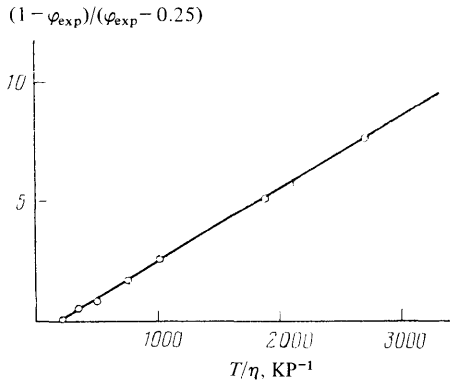


Figure 5. Dependence of $(1 - \phi_{exp})/(\phi_{exp} - 0.25)$ on T/η according to Eqn.(47) in the region of low fluidities.[26]

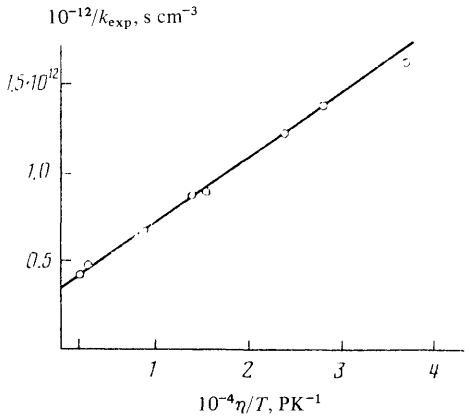


Figure 6. Dependence of $1/k_{exp}$ on η/T according to Eqn.(49) in the region of high fluidities.[26]

Geminate recombination. The kinetics of the geminate recombination of the indandionyl radicals, which have been observed only in a viscous medium (see Fig.4), obey Eqn.(31).[26] In this equation k_1 should be replaced by the constant k^*, which can have the significance of k_1^* or k_S^* depending on the state in which the geminate pair was generated: singlet or triplet (the asterisk denotes constants referring to the geminate pair). In the latter case the recombination takes place only after the conversion of the triplet pair into the singlet pair. Using Eqn.(32), $a^2=D/R^2k^*$ is found from experimental ϕ_{exp}, after which a value of k^* satisfying Eqn.(31) is selected. For this purpose, it is convenient to employ a programmable microcalculator. Since

$$a^2=D/R^2k^*=4kT/R^3k^*6\pi\eta,$$

the plot of a^2 against T/η makes it possible to determine R^3k^*. Thus $k^* = 0.9 \times 10^6$ s^{-1} and $R = 14.5$ Å were obtained for the indandionyl radicals. The value of R found makes it possible to determine the volume recombination constants k_1 and k_S, which were quoted above.

Table 2. Probability of recombination in the encounters of the indandionyl radicals forming pairs in the singlet and triplet states (according to the data of Bagdasar'yan et al.[26]) ($R = 14.5$ Å, $k_1 = 2.7 \times 10^8$ s^{-1}, $k_S = 9.0 \times 10^6$ s^{-1}).

T/η, K P^{-1}	D/R^2, s^{-1}	Recombination probabilities		
		φ_S	φ_T	φ
5	$2.2\cdot10^5$	1	1	1
50	$2.2\cdot10^6$	0.96	0.79	0.83
500	$2.2\cdot10^7$	0.88	0.25	0.41
5000	$2.2\cdot10^8$	0.52	0.03	0.15
50000	$2.2\cdot10^9$	0.12	0	0.03

If the geminate pair arises in the singlet state, i.e. $k^* = k_1^* = 0.9 \times 10^6$ s^{-1}, then the constant k_1^* is 300 times smaller than k_1. If the geminate pair arises in the triplet state, then $k^* = k_S^*$ and the constant k_S^* is 10 times smaller than k_S. It may be that the cause of the difference between the constants is that the geminate pair has an excess energy of ~3 eV at the instant of formation and is in a highly vibrationally excited state, in contrast to the pair formed in the encounter between radicals.

The volume recombination of ketyl radical,[37] obtained by the photolysis of benzopinacone in mixtures of hexane with liquid paraffin having different fluidities (from 94400 to 410 K P^{-1}), has been investigated. Treatment of the experimental data by the method described above yielded the following constants: $k_S = 3 \times 10^8$ s^{-1} and $k_1 = 0.4 \times 10^{10}$ s^{-1}. In contrast to the indandionyl radicals, the geminate recombination of the ketyl radicals was not observed. Over the entire range of fluidities of the medium investigated, the pairs dissociate and the radicals are released into space. Evidently the pairs of ketyl radicals arise in the triplet state and their lifetime is not long enough for conversion into the singlet state. If the rate constants for the geminate and volume recombinations were identical, then geminate recombination might have been observed. Thus, as in the case of indandionyl radicals, the kinetic constants of the geminate and volume recombinations differ (or at least one of them is different).

8. The Influence of a Magnetic Field

Brocklehurst[38] was the first to put forward the idea that the influence of the magnetic field on the recombination of radicals is associated with the spin transformations in the radical pair. Later studies showed that the influence of the magnetic field is due to the Δg- and HFI-mechanisms of

the spin transformations. Certain examples of the influence of magnetic field on the recombination kinetics have been presented in reviews.[29,32] Systems for which the geminate pair constants have been determined and the influence of a magnetic field on the recombination of radicals has been observed will be considered below.

Under pulsed illumination (N_2 laser, duration of pulse 3 ns) of benzophenone (B) in solution in hexane, a hydrogen atom is transferred from hexane to a benzophenone molecule in the triplet state (^{3}B) with formation of a geminate pair in a triplet state consisting of the ketyl radical $\dot{B}H$ and the hexyl radical $\dot{R}$:[39]

$$^3B + RH \rightarrow {}^3(\dot{B}H\dot{R}) .$$

The second light pulse, emitted 38 ns after the first, induces the fluorescence of the ketyl radical. When a magnetic field whose strength is up to 8 kG is applied, the Δg interaction induces the $T_0 \rightarrow S$ transition and rapid recombination (reverse transfer of a hydrogen atom) of the singlet pair formed, which is accompanied by a decrease of the fluorescence intensity of the ketyl radical. If the HFI interaction were stronger than the Δg interaction, the opposite effect would have been obtained.

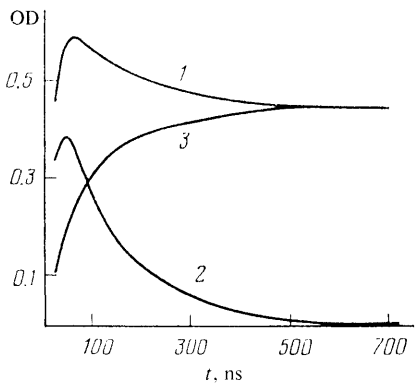


Figure 7. Kinetics of the variation of the optical density (OD) at 545 nm in the benzophenone–liquid paraffin system (η = 140 cP): 1) OD at λ = 545 nm; 2) ditto at λ = 620 nm multiplied by 3 (this is equal to the ratio $\varepsilon^{545}/\varepsilon^{620}$ for triplet benzophenone molecules); 3) difference between curves *1* and *2*.[40]

The analogous benzophenone–liquid paraffin system was investigated by nanosecond flash photolysis.[40] Fig.7 presents the kinetics of the variation of the optical density at λ = 545 nm (curve *1*) and λ = 620 nm (curve *2*) for η = 140 cP. The initial section of curve *1* is determined by the overall absorption by triplet benzophenone molecules and ketyl radicals, while the plateau on this curve corresponds to the absorption by ketyl radicals which have been released into space. Curve *2* corresponds to the absorption only by the triplet benzophenone molecules. It is seen that the triplets disappear at the instant when curve *1* reaches the plateau. Hence it follows that the destruction of the pairs $^3(\dot{B}H\dot{R})$ takes place immediately after their formation. Analysis of the experimental data leads to the conclusion that the ratio $k_d/(k_d + k_1) = 0.56$ and is independent of the viscosity of the medium. Consequently not only the dissociation of the pairs but also the transfer of a hydrogen atom from the ketyl radical to $\dot{R}$ depends on the viscosity of the medium. In the benzophenone–hexane system[39] the conversion of a triplet pair into a singlet pair competes with the dissociation of the pair. When hexane is replaced by liquid paraffin, the rate of dissociation of the pair diminishes by a factor of hundreds. Under these conditions, all the triplet pairs are converted into singlet pairs, which dissociate and recombine at approximately equal rates.

The $T-S$ transition can proceed also via the HFI-mechanism. In this case the application of a weak magnetic field decreases the probability of the $T-S$ transition as a consequence of the splitting of the triplet level and the disconnection of the T_+ and T_- states and hence decreases the fraction of the recombination process and increases the release of radicals into space. Studies of this type have been carried out in micellar solutions in which diffusional separation of the pairs is difficult, which favours spin transformations. Thus the nanosecond photolysis of various anthraquinones in a sodium dodecylsulphate solution has been studied.[41] A laser pulse results in the formation of the triplet radical pair $^3(Q\dot{R})$, where $\dot{R}$ is the radical formed from a solvent molecule and $\dot{Q}$ is a semiquinone radical. The application of a magnetic field up to 790 G slows down the destruction of the triplet pair and increases the release of the radicals into space. For anthraquinone, the constant k_S diminishes from 2.5×10^6 s^{-1} for $H = 0$ to 1×10^6 s^{-1} for H = 790 G; the constant k_d remains invariant at 1×10^6 s^{-1}.

The nanosecond photolysis of micellar solutions of benzophenone has been studied[42] in the presence of cyclohexadiene RH. A triplet pair $^3(\dot{B}H.\dot{R})$ arises under these conditions. The kinetics of the destruction of the triplet pair (it has been assumed that the destruction proceeds in accordance with a first-order reaction) and the fraction of the radicals released into space make it possible to determine the constants k_S and k_1. In a micellar solution of cetyltrimethylammonium bromide these constants are respectively 1.6×10^6 s^{-1} and 1.7×10^6 s^{-1}. The values obtained for sodium dodecylsulphate micelles are respectively 4.4×10^6 s^{-1} and 5.8×10^6 s^{-1}. When a magnetic field is applied, the release of radicals into space increases from 58% for $H = 0$ to 80% for H = 2000 G regardless of the nature of the micelles.

The spin effects and the influence of the magnetic field have been observed in the photoinitiation of emulsion polymerisation by triplet sensitisers.[43] For other methods of initiation of the emulsion polymerisation of the same monomers, the influence of a magnetic field has not been observed. The explanation is based on the considerations described above.

III. RADICAL-ION PAIRS

1. The Rehm–Weller Scheme

The behaviour of the radical-ion pairs arising as a result of the electron phototransfer will be considered in this section. The overall scheme of the phototransfer has been proposed by Rehm and Weller:[44]

$$A^* + D \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} (A \cdot D)^* \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} (A^{\dot-} \cdot D^{\dot+}) \begin{cases} \xrightarrow{k_d} A^{\dot-} + D^{\dot+} \\ \xrightarrow{k_1} A + D \end{cases} ,$$

where A* is an excited molecule of an electron acceptor, D an electron donor, (A.D)* an exciplex, i.e. an excited molecule with partial electron transfer or an excited unrelaxed acceptor–donor complex, and $(A^{\dot-}.D^{\dot+})$ a radical-ion pair

which can either recombine (reverse electron transfer) or can dissociate with formation of "free ions". The electron donor can also behave as an excited molecule. In order to complete this scheme, it is necessary to take into account the spin state of both the excited molecule and the radical-ion pair and also the possibility of the spin evolution of the pair. Thus in the phototransfer of an electron from dimethylaniline to an excited pyrene molecule in the singlet state, a radical-ion pair is produced in the excited singlet state, while the phototransfer of an electron with participation of a triplet benzophenone molecule leads to the formation of a pair in the triplet state. The energetic conditions necessary for the electron phototransfer and also the properties of the exciplexes have been examined in detail in a series of reviews and monographs[45,46] and will not be discussed in this paper. Here it is sufficient to note that, with increased dielectric constant of the medium ε, the lifetime of the exciplexes τ diminishes and there is a sharp increase of the rate constant k_e for the conversion of exciplexes into radical-ion pairs, as can be seen from Table 3.[47]

Table 3. Kinetic constants for the dimethylaniline–pyrene exciplex.[47]

Solvent	ε	τ, ns	$10^{-6}k_e$, s^{-1}
Acetonitrile	38	2.0	490
Methanol	33	9.4	95
Ethanol	24.5	19.8	41
Isopropyl alcohol	15.7	72.5	5
Tetrahydrofuran	4.6	102	~1
Diethyl ether	4.3	134.5	~1

On the basis of the Rehm–Weller scheme, we can obtain expressions for the phenomenological fluorescence quenching constant k_Q (or the constant for the destruction of the triplet state) and for the liberation of free ions. We shall assume that the process involving k_{32} can be neglected, i.e. that the vibrational relaxation is fairly rapid after the electron transfer (the process involving k_{23}). Under the conditions of steady-state illumination, stationary concentrations of the A*, (A.D)*, and ($A^{\cdot-}.D^{+\cdot}$) species are established in the solution. Having formulated the equations for the stationary state for the short-lived species indicated, in accordance with the above scheme, we arrive at the following expression for the quenching of the fluorescence (or the destruction of triplet states):

$$\frac{L_0}{L} = 1 + \frac{k_{12}\tau[D]}{1 + k_{21}/k_{23}} , \qquad (50)$$

where L_0 and L are the fluorescence intensities in the absence and presence of a quenching agent respectively and τ is the lifetime of the molecule A*. The empirical Stern–Volmer constant is expressed in terms of the constants for elementary processes in the following manner:

$$k_Q = \frac{k_{12}}{1 + k_{21}/k_{23}} . \qquad (51)$$

An expression for the quantum yield in the formation of free ions γ_{fi} can be obtained analogously:

$$\gamma_{fi} = \frac{\alpha_{fi}k_{12}\tau[D]}{1 + k_{12}\tau[D] + k_{21}/k_{23}} , \qquad (52)$$

where $\alpha_{fi} = k_d/(k_d + k_1)$ is the probability of the formation of free ions from the radical-ion pair. Two extreme cases must be considered.

1. The electron transfer is slow, i.e. $k_{21}/k_{23} \gg 1$. We then obtain

$$L_0/L = 1 + k_{12}k_{23}\tau[D]/k_{21} , \qquad (53)$$

$$\gamma_{fi} = \alpha_{fi}k_{12}k_{23}\tau[D]/k_{21} . \qquad (54)$$

2. The electron transfer is rapid, i.e. $k_{21}/k_{23} \ll 1$. We then have

$$L_0/L = 1 + k_{12}\tau[D] , \qquad (55)$$

$$\gamma_{fi} = \frac{\alpha_{fi}k_{12}\tau[D]}{1 + k_{12}\tau[D]} . \qquad (56)$$

We may note that for long lifetimes of A* ($\tau > 10^{-7}$ s) and for high values of the product $k_{12}[D] \geq 10^8$ s^{-1}, we have $k_{12}\tau[D] \gg 1$ and $\gamma_{fi} = \alpha_{fi} = k_d/(k_d + k_1)$, i.e. the quantum yield in the formation of free ions is equal to the probability of the formation of such ions from the radical-ion pair. This is the highest possible value of γ_{fi}.

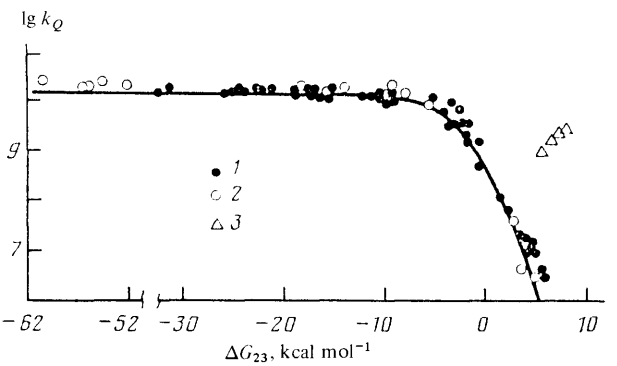


Figure 8. Dependence of the fluorescence quenching constant on ΔG_{23}: 1) electron acceptor in an excited state; 2) electron donor in an excited state; 3) transfer of a hydrogen atom.[48]

There is an interesting relation between the free energy of the electron transfer ΔG_{23} and the logarithm of the quenching constant $\lg k_Q$. The electron transfer rate constant k_{23} can be formulated in the usual form:

$$k_{23} = B_{23}\exp(-\Delta G_{23}^{\neq}/RT) , \qquad (57)$$

where B_{23} is a constant. According to Eqn.(44), $\Delta G_{23}^{\neq}$ is related to the free energy of electron transfer ΔG_{23}. The relation between these quantities can be most simply represented in the form of the linear Brønsted–Polanyi relation:

$$\Delta G_{23}^{\neq} = b + \beta\Delta G_{23} \qquad (58)$$

where b and β are constants for the given series of isotypical reactions. Thus Eqn.(57) can be written in the form

$$k_{23} = B\exp(-\beta\Delta G_{23}/RT) , \qquad (59)$$

where B is a new constant. Together with Eqn.(51), we obtain

$$k_Q = \frac{k_{12}B}{B + k_{21}\exp(\beta\Delta G_{23}/RT)} . \qquad (60)$$

For high negative values of ΔG_{23}, namely $\Delta G_{23} \leqslant -32$ kJ mol^{-1}, $k_Q = k_{12}$ follows from Eqn.(60). For positive values of ΔG_{23}, when the second term in the denominator is much greater than B, we obtain

$$\lg k_Q = \text{const} - 0{,}434\beta\Delta G_{23}/RT. \qquad (61)$$

Fig.8 presents the dependence of $\lg k_Q$ on ΔG_{23},[48] where $\beta = 0.63$ (Bagdasar'yan[49]) and $k_{12} = 2 \times 10^{10}$ litre mol^{-1} s^{-1} (diffusion constant). The relation illustrated in Fig.8 is very general and has been established for many systems with electron transfer.[45]

2. The Absolute Rate Constants for the Formation and Dissociation of Radical-ion Pairs

In the previous Section we considered conditions determining the kinetics of the formation of geminate radical-ion pairs. The rate constant for the formation of radical-ion pairs in an encounter in space is defined by the Debye formula,[7] which is obtained from Eqn.(14) for the diffusion flux by adding to the right-hand side the term which defines the flux of point particles to a spherical surface $4\pi x^2$ under the influence of Coulombic attraction (or repulsion) to the central ion. For unlike charges e_1 and e_2 in a medium with a dielectric constant ε, this flux is

$$(De_1e_2/kT\varepsilon x^2) \cdot 4\pi x^2,$$

where $e_1e_2/\varepsilon x^2$ is the Coulombic interaction force and D/kT the mobility of the ions expressed in terms of the diffusion coefficient by the Einstein formula. Thus, instead of Eqn.(14), we obtain

$$\Phi = 4\pi x^2 D \frac{\mathrm{d}c}{\mathrm{d}x} - 4\pi Dqc \ , \qquad (62)$$

where $q = e_1e_2/\varepsilon kT$ and Φ is independent of x. Integration of this equation subject to the boundary conditions $c = 0$ when $x = R$ and $c = c_\infty$ when $x \to \infty$ leads to the expression

$$\Phi = \frac{4\pi RDqc_\infty}{(\mathrm{e}^{q/R} - 1)R} = 4\pi RDpc_\infty \ , \qquad (63)$$

where

$$p = q[R(\mathrm{e}^{q/R} - 1)]^{-1}$$

is the correction to Smoluchowski's formula for the number of encounters. The quantity q/R is the ratio of the Coulombic and thermal energies and Φ/c_∞ represents the rate constant for the encounters of radical-ions.

Eigen[50] obtained an expression for the rate of diffusional dissociation from the condition for the diffusional equilibrium of radical-ion pairs:

$$4\pi RDp[\mathrm{A}][\mathrm{D}] = k_\mathrm{d}[\mathrm{A}\cdot\mathrm{D}]_\mathrm{eq} \qquad (64)$$

The equilibrium concentration of the pairs is obtained from Eqn.(8) by introducing the Boltzmann multiplier $e^{-q/R}$, which leads to the equation

$$k_\mathrm{d} = \frac{D}{R^2}\left(\frac{q/R}{1 - \mathrm{e}^{-q/R}}\right) \ , \qquad (65)$$

where the multiplier in brackets represents the correction to the diffusion dissociation constant D/R^2 of uncharged species. It is noteworthy that Eqns.(63) and (65) presuppose that the ions are separated by at least one solvent molecule.

3. Geminate Radical-ion Pairs

The behaviour of the geminate radical-ion pairs arising as a result of electron phototransfer has recently attracted much attention. The influence of magnetic field on the yield of particular final recombination products has been studied in a number of investigations. However, the kinetic constants of the elementary processes determining the behaviour of the radical-ion pairs have been found in only a few studies. We shall consider in greater detail some of the systems investigated.

1. Pyrene–aromatic amines.[47,51–55] On excitation of pyrene (Py) with a laser pulse in the presence of a high concentration (0.1 M) of dimethylaniline (D) in a polar medium (CH_3OH or CH_3CN), an exciplex in a singlet state $^1(\mathrm{Py.D})^*$ is formed. The subsequent processes in this system are indicated schematically below:

$$\begin{array}{l} \mathrm{Py} + \mathrm{D} \rightarrow {}^1(\mathrm{Py}\cdot\mathrm{D})^* \longrightarrow \mathrm{Py} + \mathrm{D} \\ \quad\quad\quad\

yield of the free ions on the viscosity of the medium was established:[55] with increase of the viscosity by a factor of 25 (from 5.8 to 142 cP), the constant k_d decreased only by a factor of 4 (from 2.6×10^7 to 0.6×10^7 s^{-1}). Experimental data were anlaysed in the above study without taking into account the spin transitions.

2. Anthracene–dimethylaniline (D).[56] The anthracene in solution in acetonitrile was excited with light at $\lambda = 337$ nm (N_2 laser, duration of pulse 2.5 ns). At a dimethylaniline concentration of 0.1 M, the fluorescence of anthracene is fully quenched after only 1 ns, which leads to the formation of a radical-ion pair in the singlet state. The kinetics of formation of the triplet anthracene molecule ^3A were determined by probing the solution at $\lambda = 425$ nm (the absorption maximum of ^3A). The probing beam from a dye-based laser followed the exciting beam at different time intervals. In the absence of a magnetic field, the yields of the anthracene triplets were 4.8, 8.2, and 10.5% after 5, 7, and 15 ns respectively. After the application of a magnetic field, the yield of the triplets diminished and reached a limiting value in fields stronger than 150 G. Subject to certain assumptions, agreement was achieved between the experimental data and the theory of spin evolution induced by hyperfine interaction.[53]

3. Fluorenone–diazabicyclo-octane in propylene carbonate.[57] Under the influence of light at $\lambda = 347$ nm (ruby laser), a triplet fluorenone molecule and then a radical-ion pair in the triplet state are formed. Optical absorption by the fluorenone triplets at 425 nm was measured immediately after the laser pulse and when 2 μs had elapsed, measurements were also made of the absorption by the fluorenone radical-anions at 540 nm. The fraction of the triplet radical-ion pairs which have dissociated into ions was determined from these data. The viscosity of propylene carbonate was varied from 1 to 100 cP by varying the temperature from 213 to 343 K. In this range of viscosities the yield of free ions α_{fi} changed from 0.13 to 0.89. It was assumed that the free ions are formed on dissociation of the triplet pair and that the recombination (reverse electron transfer) takes place in the singlet pair after the change in the spin state of the pair. Thus $\alpha_{fi} = k_d/(k_d + k_S)$ and, after the application of a magnetic field, $\alpha_{fi}^H = k_d/(k_d + k_S^H)$. The influence of the magnetic field can be represented in the form $(\alpha_{fi}^H - \alpha_{fi})/\alpha_{fi}$. This ratio increases from 1.5% to 23% with increase of the viscosity of the medium from 1 to 45 cP ($H = 270$ G). After the application of the magnetic field, the T_+ and T_- sublevels are disconnected, which decreases the probability of the transition from the triplet to the singlet pair and increases the probability of the competing process—the dissociation of the triplet pair into free ions.

The dependence of the probability of recombination $\phi = 1 - \alpha_{fi}$ on the viscosity of the medium has also been examined by the Noyes method.[57] The application of the diffusion gradient method makes it possible to estimate the constant k_S. Fig.9 illustrates the dependence of $1/\alpha_{fi}$ on η/T according to the data of Periasamy and Linschitz:[57] $k_S = 3 \times 10^8$ s^{-1} follows from the slope.

4. Pyrene–dicyanobenzene (A) in various solvents.[58] Excitation with a laser pulse at $\lambda = 347$ nm results in the formation of the radical-ion pairs ($Py^+.A^-$). The kinetics of the formation and destruction of the radical-ion pairs and the free Py^+ ions were followed spectrophotometrically at 445 nm (the absorption maximum of Py^+), while the kinetics of the formation and destruction of the free ions alone were followed conductimetrically (for several hundreds of nanoseconds). In solutions in acetonitrile ($\varepsilon = 38$) the maximum photocurrent is obtained immediately after the termination of the pulse and then diminishes slowly as a consequence of volume recombination. With decrease of ε of the solvent, the maximum photocurrent is attained after a longer time as a consequence of the decreased rate of dissociation of the radical-ion pairs. For liquids of average polarity ($\varepsilon = 9$–12), the experimental rate of formation of free ions approximately agrees with the rate of dissociation of the radical-ion pairs calculated by Eqn.(65).

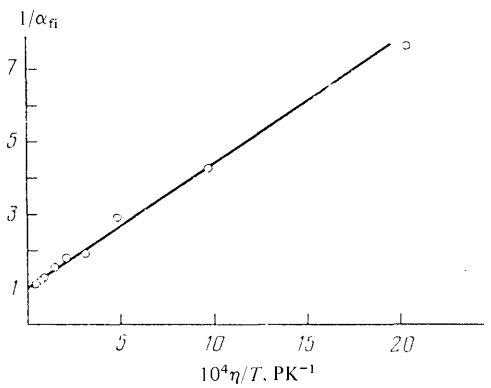


Figure 9. Dependence of $1/\alpha_{fi}$ on η/T according to the data of Periasamy and Linschitz.[57]

5. The

$Ru^{2+}(bpy)_3$ – methylviologen $\left(CH_3-\overset{+}{N}\!\!\bigcirc\!\!-\!\!\bigcirc\!\!\overset{+}{N}-CH_3\right)$.

system. This system has been the subject of numerous investigations in connection with the problem of the photochemical utilisation of solar energy, since, on illumination with visible light, it is thermodynamically feasible for the system to allow the decomposition of water into hydrogen and oxygen.[49] The primary reaction leads to the formation of a radical-ion pair (MV^{2+} = methylviologen):

$$Ru^{2+}(bpy)_3^* + MV^{2+} \rightarrow [Ru^{3+}(bpy)_3 \cdot MV^+] \begin{cases} \xrightarrow{k_1} Ru^{2+}(bpy)_3 + MV^{2+} \\ \xrightarrow{k_d} Ru^{3+}(bpy)_3 + MV^+ \end{cases}.$$

The radical-ion pair either recombines or dissociates with formation of the free ions MV^+ and $Ru^{3+}(bpy)_3$, which, in the presence of catalysts, are capable of inducing the evolution of hydrogen and oxygen respectively from water.

The yield of free ions from the radical-ion pairs, i.e. the quantity $k_d/(k_d + k_1)$, has been determined[59] by the method of nanosecond photolysis ($\lambda = 530$ nm). A characteristic feature of this system is the long lifetime of the excited $Ru^{2+}(bpy)_3^*$ molecules (several hundreds of nanoseconds), during which pairs are continuously generated and destroyed. The concentration of the radical-ions MV^+ released into space is related to the concentration of $Ru^{2+}(bpy)_3^*$ formed during the pulse in the following manner:

$$[MV^+]_\infty = [Ru^{2+}(bpy)_3^*] \frac{k_2[MV^{2+}]}{k_0 + k_2[MV^{2+}]} \frac{k_d}{k_d + k_1}, \qquad (66)$$

where the first fraction represents the probability of the reaction of $Ru^{2+}(bpy)_3^*$ with MV^{2+} [k_0 is the rate constant for the spontaneous deactivation of $Ru^{2+}(bpy)_3^*$]. All the necessary quantities were determined experimentally. Thus the

probability of the relase of the radical-ions into space from the radical-ion pairs was determined from Eqn.(66); it amounts to 0.22 for an aqueous solution and to 0.17 for an aqueous glycerol solution (η = 3.3 cP).

---o0o---

The application of diffusion kinetics to the description of homogeneous molecular processes began with the studies of Vavilov and co-workers (1928–1929), who based their treatment on the diffusion theory of the rapid coagulation of colloids proposed by Smoluchowski (1918). These studies led to the development of the diffusion gradient method for the description of the recombination of radicals and other barrier-free processes. Franck and Ravinowitch (1934) put forward the concept of the "cage" in which a "pair" of radicals arising in the photochemical or thermal dissociation of the molecules is enclosed. In Noyes' studies (1955–1961) the pair was regarded as a dynamic system whose behaviour is described by the microscopic parameters of molecular movement. Subsequently a quantitative description of the cage effect based on phenomenological kinetic parameters was achieved using the gradient diffusion method. This led subsequently to the concept of contact or "almost" contact pairs as intermediate species in radical-barrier free reactions.

The discovery of the spin and magnetic effects in radical pairs is a new important stage in a development of our ideas about the recombination of radicals. Soviet scientists have made a considerable contribution to the development of these ideas. The creation of a rigorous quantitative theory of the recombination of radicals taking into account the spin and magnetic effects and the molecular movements of radicals constitutes a very complex problem. An important step in this direction was made as a result of studies published recently.[60,61]

An approximate method, which the author of the present review called the approximation of chemical kinetics, has been widely used in experimental studies on the recombination of radicals. The phenomenological rate constants for various elementary processes, including diffusion and spin processes, which together determine the behaviour of the radical pairs, are used in this method. These constants can be found from experimental data.

The theory of radical recombination is still far from being complete. The experimental data considered in this review indicate an appreciable difference between the kinetic constants for geminate pairs and the pairs formed in the enounters of the same radicals in space. The discrepancy is apparently associated with the characteristic features of the formation and behaviour of the geminate pairs. It is undoubtedly essential to take into account the rotational diffusion of the radicals forming the contact or "almost" contact pairs, to which attention has been drawn in the present review. The recombination and dissociation of the radical-ion pairs and their dependence on the viscosity of the medium have been inadequately studied. The Debye–Smoluchowski [Eqn.(63)] and Eigen [Eqn.(65)] equations have received little experimental confirmation for organic radical-ions. Thus this field of chemical kinetics requires further studies—both experimental and theoretical.

The behaviour of geminate electron–radical-cation pairs, which were mentioned in the Introduction, is of considerable interest. The properties of these pairs to a large extent determine the chemical reactions occurring under the influence of ionising radiation on liquid media. A convenient method for the study of these pairs is two-quantum photoionisation (see the present author's earlier review[62]). The high mobility of electrons in the liquid medium results in a significant difference between an electron–radical-cation pair and a radical ion pair. The properties of geminate electron–radical-cation pairs therefore require separate consideration.

REFERENCES

1. R.M.Noyes, "Progress in Reaction Kinetics", Pergamon Press, 1961, Vol.1, p.129.
2. K.Razi Naqvi, K.J.Mork, and S.Waldenstrom, J.Phys.Chem., 1980, **84**, 1315.
3. M.Smoluchovski, Z.phys.Chem., 1918, **92**, 129.
4. S.I.Wawilow, Z.Phys., 1928, **50**, 52.
5. Kh.S.Bagdasar'yan, Zhur.Fiz.Khim., 1967, **41**, 1679 [Russ.J.Phys.Chem., 1967(7)].
6. Kh.S.Bagdasar'yan, Kinetika i Kataliz, 1983, **24**, 719.
7. P.Debye, Trans.Electrochem.Soc., 1942, **82**, 265.
8. S.I.Wawilow, Z.Phys., 1929, **53**, 665.
9. J.Franck and E.Rabinowitch, Trans.Faraday Soc., 1934, **30**, 120.
10. E.T.Denisov, "Kinetika i Kataliz (Itogi Nauki i Tekhniki)" [Kinetics and Catalysis (Advances in Science and Engineering)], Izd.VINITI, Moscow, 1981, Vol.9.
11. J.K.Kochi (Editor), "Free Radicals", Wiley Intersci., New York, 1973, p.157.
12. Kh.S.Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd.Nauka, Moscow, 1966.
13. O.D.Trapp and G.S.Hammond, J.Amer.Chem.Soc., 1959, **81**, 4876.
14. L.F.Meadows and R.M.Noyes, J.Amer.Chem.Soc., 1960, **82**, 1870.
15. O.Dobis, J.M.Pearson, and M.Szwarc, J.Amer.Chem. Soc., 1968, **90**, 278.
16. G.S.Hammond and J.R.Foz, J.Amer.Chem.Soc., 1964, **86**, 1918.
17. E.Niki and Y.Kamiya, J.Amer.Chem.Soc., 1974, **96**, 2129.
18. K.Chakravorty, J.M.Pearson, and M.Szwarc, J.Amer. Chem.Soc., 1968, **90**, 283.
19. J.M.Teddor and J.C.Walton, "Progress in Reaction Kinetics", Pergamon Press, New York, 1967, Vol.14, p.37.
20. S.King Wong, Int.J.Chem.Kinetics, 1981, **13**, 433.
21. S.W.Benson, "The Foundations of Chemical Kinetics" (Translated into Russian), Izd.Mir, Moscow, 1964, p.467.
22. T.J.Chuang, G.W.Hoffman, and K.B.Eisenthal, Chem.Phys.Letters, 1974, **25**, 201.
23. D.F.Kelley and P.M.Rentzepis, Chem.Phys.Letters, 1982, **85**, 25.
24. J.C.Dutoit, J.M.Zellweger, and H.Bergh, J.Chem. Phys., 1983, **78**, 1825.
25. J.V.Khudyakov, Yu.I.Kiryukhin, and A.I.Yasmenko, Chem.Phys.Letters, 1980, **74**, 462.
26. Kh.S.Bagdasar'yan, Yu.I.Kiryukhin, and Z.A.Sinitsyna, Khim.Fiz., 1982, 1666.
27. Kh.S.Bagdasar'yan, Dokl.Akad.Nauk SSSR, 1981, **258**, 1133.
28. A.L.Buchachenko, "Khimicheskaya Polyarizatsiya Elektronov i Yader" (Chemically Induced Electron and Nuclear Polarisation), Izd.Nauka, Moscow, 1974.

29. R.Z.Sagdeev, K.M.Salikhov, and Yu.N.Molin, Uspekhi Khim., 1977, **46**, 569 [Russ.Chem.Rev., 1977(4)].
30. O.A.Anisimov, V.L.Bizyaev, N.N.Lukzen, V.M.Grigoryants, and Yu.N.Molin, Dokl.Akad.Nauk SSSR, 1983, **272**, 383.
31. B.Brocklehurst, J.Chem.Soc., Faraday Trans.II, 1976, **72**, 1869.
32. A.L.Buchachenko, "Fizicheskaya Khimiya. Sovremennye Problemy" (Physical Chemistry. Modern Problems), Izd.Khimiya, Moscow, 1980, p.7.
33. A.L.Buchachenko and V.L.Berdinskii, Uspekhi Khim., 1983, **52**, 3 [Russ.Chem.Rev., 1983(1)].
34. A.L.Buchachenko, E.M.Galimov, V.V.Ershov, G.A.Nikiforov, and A.D.Pershin, Dokl.Akad.Nauk SSSR, 1976, **228**, 379.
35. N.J.Turro and B.Kraeutler, Acc.Chem.Res., 1980, **13**, 369.
36. A.L.Buchachenko and A.M.Vasserman, "Stabil'nye Radikaly" (Stable Radicals), Izd.Khimiya, Moscow, 1973, p.361.
37. V.A.Borovkova and Kh.S.Bagdasar'yan, Dokl. Akad.Nauk SSSR, 1983, **269**, 132.
38. B.Brocklehurst, Nature, 1969, **221**, 321.
39. H.Staerk and K.Razi Naqui, Chem.Phys.Letters, 1977, **50**, 386.
40. V.A.Borovkova, Yu.I.Kiryukhin, and Kh.S.Bagdasar'yan, Khim.Fiz. (In the press).
41. Y.Tanimoto, H.Udagawa, and M.Itoh, J.Phys.Chem., 1983, **87**, 724.
42. J.C.Scaiano, E.B.Abnin, and L.C.Stewart, J.Amer. Chem.Soc., 1982, **104**, 5673.
43. N.J.Turro, M.-F.Chow, C.-J.Chung, and C.-H.Tung, J.Amer.Chem.Soc., 1983, **105**, 1572.
44. D.Rehm and A.Weller, Ber.Bunsenges.Phys.Chem., 1969, **73**, 834.
45. A.K.Chibisov, Uspekhi Khim., 1981, **50**, 1169 [Russ. Chem.Rev., 1981(7)].
46. A.I.Kryukov, V.P.Sherstyuk, and I.I.Dilung, "Fotoperenos Elektrona i Ego Prikladnye Aspekty" (Electron Phototransfer and Its Applied Aspects), Izd.Naukova Dumka, Kiev, 1982.
47. A.Weller, Z.phys.Chem.(Frankfurt), 1982, **130**, 129.
48. D.Rehm and A.Weller, Isr.J.Chem., 1970, **8**, 259.
49. Kh.S.Bagdasar'yan, Khim.Fiz., 1982, 391.
50. M.Eigen, Z.phys.Chem.(Frankfurt), 1954, **1**, 176.
51. N.Orbach, R.Potashinik, and M.Ottolenghi, J.Phys. Chem., 1972, **76**, 1133.
52. H.J.Werner, H.Staerk, and A.Weller, J.Chem.Phys., 1978, **68**, 2419.
53. W.Bube, R.Haberkorn, and M.E.Michel-Beyerle, J.Amer.Chem.Soc., 1978, **100**, 5993.
54. D.M.Goodall, N.Orbach, and M.Ottolenghi, Chem. Phys.Letters, 1974, **26**, 365.
55. V.I.Kiryukhin, V.A.Borovkova, Z.A.Sinitsyna, and Kh.S.Bagdasar'yan, Dokl.Akad.Nauk SSSR, 1984, **274**, 114.
56. M.E.Michel-Beyerle, H.W.Krüger, and R.Haberkorn, Chem.Phys., 1979, **42**, 441.
57. N.Periasamy and H.Linschitz, Chem.Phys.Letters, 1979, **64**, 281.
58. T.H.Masuhara and N.Mataga, Bull.Chem.Soc.Japan, 1976, **49**, 394.
59. V.A.Borovkova, Yu.I.Kiryukhin, Z.A.Sinitsyna, and Kh.S.Bagdasar'yan, Khim.Vys.Energii (In the press).
60. V.A.Belyakov and A.L.Buchachenko, Khim.Fiz., 1983, 1510.
61. V.A.Belyakov and A.L.Buchachenko, Khim.Fiz., 1983, 1385.
62. Kh.S.Bagdasar'yan, Symposium, "Vozbuzhdennye Molekuly. Kinetika Prevrashchenii" (Excited Molecules. Reaction Kinetics), Izd.Nauka, Leningrad, 1982, p.117.

Karpov Physicochemical Institute,
Moscow