

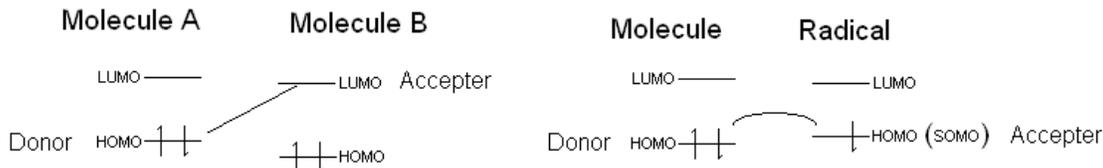
The donor-acceptor bond and free radicals – radical pairs, complexes of free radicals,  
mechanisms of chemical reactions.

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In the article it is argued as the donor-acceptor interaction of two free radicals, as well as  
the donor-acceptor interaction between a free radical and a neutral spin-paired molecule  
can explain many different phenomena in EPR-spectroscopy and in the mechanisms of  
the chemical reactions.

## 1.Theoretical introduction.

The donor-acceptor interaction is familiar in chemistry, and can be well described from the point of view of quantum mechanics [1]. This interaction is best known for pairs of molecules that do not have free valency, for example, the complex of molecular iodine acting as an acceptor, and benzene as a donor. As I will argue, it follows from general consideration of quantum mechanics that free radicals should give rise to charge-transfer complexes especially easily. It also follows, that for the complexes between free radicals and spin-paired molecule, the free radical is likely to be an electron acceptor. Consider the levels involved in a typical interaction between two molecules (at left in Fig.1) and a molecule and a radical (right).



**Fig.1**

**A schematic drawing of the upper energy levels of a molecule interacting with another molecule (left) and a molecule interacting with a free radical (right). The straight (left) or curved (right) line indicates the charge-transfer interaction. This is schematic representation (from the point of view of method MO LCAO) of the interaction in the charge transfer complex between the two molecules (both of them spin-paired on the left) and the interaction between the molecule and the free radical on the right. HOMO means the highest occupied molecular orbital, LUMO means the lowest unoccupied molecular orbital and HOMO called SOMO (single**

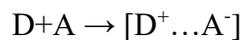
**occupied molecular orbital) in the case of free radical. It is possible to see, that in the second case the electron transfer costs little or no energy (in some hypothetical “averaged” case, of course) while in the case of the complex between the hypothetical “averaged” spin-paired molecules it is always a comparable gap between the LUMO and the HOMO. This simple picture shows that free radicals should form charge transfer complexes (or a hydrogen bond complexes, treated similarly, very easily)**

In this schematic picture HOMO refers to the highest unoccupied molecular orbital (typically called SOMO, (single occupied molecular orbital) in the case of free radical), LUMO means the lowest unoccupied molecular orbital. While the details may depend on the orbital energies involved, Fig.1 shows pretty typical case. The figure makes it clear that the energy gap between orbital involved in a molecule-radical donor-accepter interaction is smaller than for a molecule-molecule complex. The radical should in general be a very good acceptor in any such interaction. Comparison of the ionization potentials for the similar organic radical and molecules confirms, that despite SOMO for radical lies a little higher in energy, than HOMO of the parent molecule, this difference is much less, than the difference between HOMO and LUMO (again, it is true for similar compounds, because in principle it is always possible to find a strong acceptor and a radical, that serves as a donor). For example, for phenol ionization potential is 8.46 eV

[2] versus 8.5 eV for  $\cdot\text{OC}_6\text{H}_5$  [3], for benzene ionization potential is 9.8 eV [4] versus 9.9 eV for  $\cdot\text{C}_6\text{H}_5$  [3], for toluene ionization potential is 8.82 eV [5] versus 7.7 eV for  $\cdot\text{CH}_2\text{C}_6\text{H}_5$  [3] (the difference is still smaller than the difference between HOMO and LUMO, approximately equal to energy of chemical bond  $\sim 2-3$  eV).

The main property of free radicals is that they may recombine (if steric environment allow it) with bond formation. The above argument that free radical should also be characteristically strong acceptor in a charge-transfer interaction, can also be developed in another way, using the classical Milliken approach.

Consider the charge-transfer complex of a type:



For this complex it is possible to write its wave function in the form [1,6]:

$$\Psi([DA]) = a\Psi(D+A) + b\Psi([D^+ \dots A^-]) = a\Psi_o + b\Psi_{ct} \quad (a \gg b)$$

The energy  $E$  of the system can be expressed with the help of the formula:

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle a\Psi_o + b\Psi_{ct} | H | a\Psi_o + b\Psi_{ct} \rangle}{\langle a\Psi_o + b\Psi_{ct} | a\Psi_o + b\Psi_{ct} \rangle}$$

where  $H$  is an effective Hamiltonian for the system.

The condition of the minimum of the energy yields the first equation for  $a, b$ :

$$\delta W / \delta a = 0$$

$$-aH_{00}(aS+b) + H_{11}b(a+bS) + H_{01}(a^2 - b^2) = 0$$

Here  $H_{00}$ ,  $H_{11}$ ,  $H_{01}$ ,  $S$  are the following integrals:

$$H_{00} = \int \Psi_o H \Psi_o d\tau; H_{01} = \int \Psi_o H \Psi_{ct} d\tau; H_{11} = \int \Psi_{ct} H \Psi_{ct} d\tau; S = \int \Psi_o \Psi_{ct} d\tau.$$

( $H_{00}$  corresponds to the energy of the initial state before the electron transfer,  $H_{11}$  – after

the energy transfer,  $H_{01}$  – interaction energy,  $S$  – overlap integral)

Normalization of the wave function yields the second equation for  $a, b$ :

$$a^2 + b^2 + 2abS = 1$$

After rewriting the first equation:

$$-a^2 H_{00} S - ab H_{00} + ab H_{11} + b^2 S H_{11} + a^2 H_{01} - b^2 H_{01} = 0$$

For illustrative example simplification can be made: overlap integral  $S=0$ , then:

$$-ab H_{00} + ab H_{11} + a^2 H_{01} - b^2 H_{01} = 0$$

And since  $a \gg b$ , the member with  $b^2$  also can be omitted, that allows to estimate the ratio

$b/a$ :

$$|b/a| \sim |H_{01}/(H_{00}-H_{11})|$$

From that formula it is seen, that if  $H_{00} \sim H_{11}$ , that is, at the production of the donor-acceptor bond there is no essential increase of the energy of the system (the electron is not climbing from HOMO to LUMO, see Fig.1), then the value of  $|b/a|$  will be large, and, therefore the admixture of the charge-transfer state (and, therefore, the bond between the radical and the molecule) will be strong (the case on the right). If, however the difference  $|H_{11}-H_{00}|$  is large (the case to the left), then even if  $H_{01}$  is large, the  $|b/a|$  is small and the bond is weak.

An analogous considerations are applicable to the case of the donor-acceptor interaction between the two radicals, in this case the two interacting orbitals will be two SOMO. Generally speaking, in the ordinary case of the interaction of two sterically unhindered radicals it would lead to the creation of the ordinary covalent bond, but, if because of the steric hindrance effect the two radicals can't approach close to each other, then the donor-acceptor interaction (more long distant than the covalent bond) will still give the bond between the radicals. The question is: will the spin condition of that radical pair be singlet or triplet? The answer is: the lowest state is still singlet, because for the

symmetric coordinate wave function the spin state is singlet, but because of the peculiarities of the bond the triplet state will be very close in energy. Since the donor-acceptor interaction yields the bond at a larger distance compare to covalent bond, then the exchange integral for the state  $\Psi_0$ , that is responsible for energy separation between the singlet and the triplet levels, will be small (indeed, for the case of the ordinary radical pair, when the two radicals are well separated, they always give EPR-signal of the radical pair, despite the singlet state is still lower in energy). At this case the singlet-triplet splitting for the state  $\Psi_1$  (when the electron is completely transferred) can be very large, but this is not influencing the singlet-triplet splitting for the state  $\Psi_0$ .

In order to better explain the fact, that singlet-triplet splitting indeed does not grow in the case of the production of the donor-acceptor bond, it is necessary to calculate the exchange integral directly:

$$H_{ex} = (a\Psi_1(1)\Psi_2(2) + b\Psi_1(1)\Psi_1(2))H(a\Psi_1(2)\Psi_2(1) + b\Psi_2(1)\Psi_2(2))$$

Here the wave function of the initial state is written as  $\Psi_o = \Psi_1(1)\Psi_2(2)$  (it means the 1<sup>st</sup> electron is on the first radical, the second electron is on the second radical), and the wave function of the state with charge transfer is written as  $\Psi_{ct} = \Psi_1(1)\Psi_1(2)$  (first electron on the first radical and the second electron is also on the first radical). Correspondingly the complimentary to them state can be written as  $\Psi_o = \Psi_2(1)\Psi_1(2)$  (the first electron is on the second radical and the second electron is on the first radical) and  $\Psi_{ct} = \Psi_2(1)\Psi_2(2)$  (the first electron is on the second radical and the second electron is also on the second radical). Calculations of the exchange integral yields:

$$H_{ex} = a^2 \langle \Psi_1(1)\Psi_2(2) | H | \Psi_1(2)\Psi_2(1) \rangle + ab \langle \Psi_1(1)\Psi_2(1) | H | \Psi_2(1)\Psi_2(2) \rangle +$$

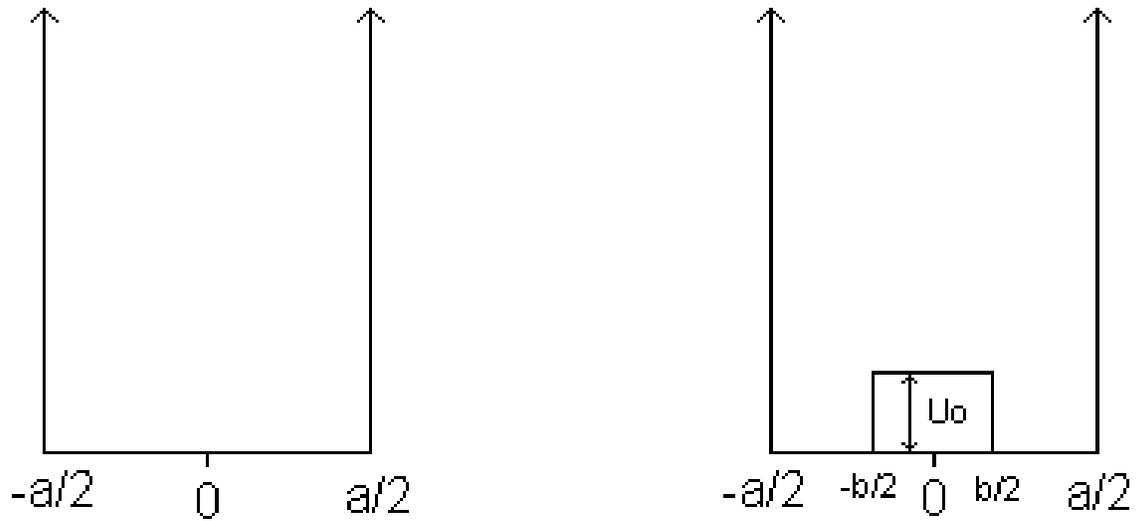
$$ab \langle \Psi_1(1)\Psi_1(2) | H | \Psi_2(1)\Psi_2(2) \rangle + b^2 \langle \Psi_1(1)\Psi_1(2) | H | \Psi_2(1)\Psi_2(2) \rangle \sim a^2 H_{oex}$$

The first member is the exchange integral of the initial state without charge transfer and at the large distances it is exponentially small, the second and the third members can be estimated as less than  $2ab \langle \Psi_1(1)\Psi_2(1) \rangle \times (2E_o + \text{small integrals})$

depending on distance between the radicals) =  $2abS_0(2E_0 + \text{small integrals})$ . Here  $E_0$  is the initial energy of the radical (that is, of course, a large value), but it is multiplied by  $S_0$  (overlapping integral between the radicals) and  $b \ll a$ , therefore, very small. The last member, according to [6] is the exchange integral of the complete electron transfer state, it is multiplied by  $b^2$  and can be neglected.

Therefore, the exchange integral for the radical pair of association, when the two radicals are connected by the state with charge transfer will be approximately coincide with the exchange integral for two radicals, that are situated at a large distance from each other. Then the triplet state will be close to the lowest singlet state and in the EPR spectrum at room temperature it will be again the EPR spectrum of the radical pair.

One more interesting proof of the fact, that the lowest singlet and triplet states in the system consisted from two radicals are close to each other in the special type of the energy well, can be obtained from the analysis of the influence onto the low lying levels of energy in the system, consisted from the rectangular well with infinitely large walls of the perturbation at the center of the well.



**Fig.2**  
**On the left – the initial one-dimensional energy well with infinite walls, on the right – the perturbation in the well, that leads to the change of energies of symmetrical and asymmetrical wave functions (see text).**

Let's suppose, that due to the donor-acceptor interaction both electrons of two radicals are trapped in a rectangular well with infinite walls and of the length  $a$  (Fig.2 on the left).

In this well the stationary Schrodinger equation gives the solutions:

$$H\Psi = E\Psi$$

$$-(\hbar^2/2m)d^2\Psi/dx^2 = 0 \text{ for } -a/2 < x < a/2, \quad \Psi = 0 \text{ for } x > a/2, \quad a/2 < x$$

The boundary conditions are:  $\Psi(-a/2) = \Psi(a/2) = 0$

The solutions are:

$\Psi_0 = A \cos(kx)$ , then  $\Psi(a/2) = A \cos(ka/2) = 0$ ,  $ka/2 = \pi/2$ ,  $k = \pi/a$ , and therefore,

$\Psi_0 = A \cos(\pi x/2)$ ; and from the Schrodinger equation  $E_0 = (\hbar^2/2m)(\pi^2/a^2)$

Normalization of that equation yields:  $A = (2/a)^{1/2}$

$\Psi_1 = B \sin(2\pi x/a)$ , then  $E_1 = (2\hbar^2/m)(\pi^2/a^2)$ , and after the normalization  $B = (2/a)^{1/2}$

If now to introduce the symmetric perturbation at the center of the well (see Fig.2

right)  $U_0 \ll E_0, E_1$ ;  $b < a$

Then the calculation of the perturbation integrals in the first order yields:

$$E_{01} = (2/a)U_0 \{ b/2 + [a/(2\pi)] \sin(\pi b/a) \}$$

$$E_{11} = (2/a)U_0 \{ b/2 - [a/(4\pi)] \sin(2\pi b/a) \}$$

For example, for  $b = a/4$  it is possible to see:

$$E_0 = (\hbar^2/2m)(\pi^2/a^2) + U_0(1/4 + (2)^{1/2}/(2\pi)) = (\hbar^2/2m)(\pi^2/a^2) + 0.4785U_0$$

$$E_1 = (2\hbar^2/m)(\pi^2/a^2) + 0.0908U_0$$

It is possible to see, that the approaching in energy takes place of the first level ( $\Psi_0$  is a symmetrical coordinate wave function, and therefore this is a singlet term) and the second term ( $\Psi_1$  is an antisymmetrical wave function, this is a triplet term). This is very easy to understand, because for the case of the symmetric function the perturbation has a high influence, since the function has the maximum in the place of the perturbation,

while for the case of antisymmetric wave function there is a nod in the place of the perturbation. And, therefore, it is possible to expect, that the electrons caught in such a double-well potential (created by the charge-transfer interaction, for example), will demonstrate a small singlet-triplet splitting.

This explanation seemingly looks like the most appropriate explanation of the existence of the radical pairs, connected by the donor-acceptor interaction on the level of the simplified quantum mechanics (point of view of chemist). Why two radicals are generating a bond, but at the same time there is still the EPR-signal is present, this time as a signal of the radical pair. From the point of view of the modern advanced methods of the quantum mechanical calculations it is better to talk about the inevitable admixture of the excited states to the ground state, what generates a bond.

## 2.Radical pairs of association.

For many years the existence of the radical pairs (two radicals in the solid, separated by some fixed distance and exhibiting the characteristic spectrum) was explained by the properties of the solid state to capture at low temperatures (normally 77 K) the radicals and to prevent recombination through the reduced mobility at low

temperature [7]. The normal mechanism of generation of that type of radical pairs is to irradiate the monocrystal of the compound by gamma-radiation at low temperature [7] or by irradiating the frozen solution of charge-transfer complexes between the quinone and pyrochatechol (or other compounds [8]). In this case the appearance of radicals trapped nearby is obvious – they just can't go away in a cryogenic matrix and are trapped in a cage. However, there are several publications in literature, when the radical pairs are observed after the evaporation of the solution, that includes the free radicals [9-12]. The EPR signal is observed in all publications, because the articles are devoted to the sterically hindered stable radicals. But why are they arranged in pairs? Why is it possible to see the signal with one exact value of the dipole-dipole interaction? Even if the clusterization of the radicals takes place (they form the separate phase at evaporation) it should be the broad exchange-narrowed singlet line due to the overconcentration of the radicals or several distances between the radicals, if the cluster is so small. More recently several new results were published, when the signals were observed for the case of the atoms trapped after the discharge in the matrixes of noble gases and there are again in some cases the distinct signals of radical pairs [13]. But even if there is no distinct signals

of the radical pairs (the fine structure is hidden under the wings of the strong signal of the monoradical [14]) it is still possible to deduce from the strong signal in a forbidden field, that this signal in a forbidden field is due to the presence of the radical pairs, radicals being associated into pairs from the atoms at freezing of the discharge beam at the noble gas matrix.

Indeed, the alternative explanation of the signal in a forbidden field would be the explanation that since the signal in the forbidden field is formed at any distance between the two radicals (since the dipole-dipole interaction always present) then at high concentration of the radical itself the signal from such statistical (accidental) pairs still will be present in the forbidden (half) field. For example, in [14,15] the spectrum EPR was observed of hydrogen atoms, captured in a matrix of the noble gas. In such an experiment the strong EPR signal of the hydrogen atoms itself was observed exactly as it should be according to the knowledge about the large hyperfine splitting and a weak, but observable signal in half field, but no signals with the fine structure near the signal for the hydrogen atoms. The authors [14] attributed that signal in a forbidden field to the radical pairs with large distance between the atoms, more than 7 Å, and the fact of the generation

of that radical pairs itself was attributed to the Van-der-Waals interaction, with the emphasis [13], that the more rigorous calculations of the force between the radicals are necessary.

The idea of the formation of the radical pairs with some distance of 7 Å and higher is close to the idea of the concentration radical pairs, that is, the radical pairs that are due to the high concentration of the radical and, therefore, due to the statistical accidental generation of pairs. In this case the signal in the forbidden field would be increased as  $n^2$  with the concentration of the radicals (see below). But in reality according to [14] the ratio of the signal of the radical pairs (measured as a signal in a forbidden field) to the signal of the hydrogen atom is approximately constant. Indeed, in [14] the level of  $H_2$ /neon was varied in a discharge and for levels of 0.09%, 0.5%, 2% the signal in a forbidden field changed as 3.3 to 5.5 to 15 (multiplication factor  $10^6$ ) and the signal in a main field changed as 2.0 to 3.1 to 6.5 (multiplication factor 10). Therefore, the relative concentration of the radical pairs with respect to the concentration of the radical almost does not change.

### 3. Concentrational radical pairs.

Since for the case of hydrogen atoms just the signal in the forbidden field is observed, it is necessary to consider the trivial possibility of generation of such a signal – the phenomenon of the appearance of the signal in the half-field, that appears as a consequence of the dipole-dipole interaction between the different spins, being considered as pairs irrespective of the distance (that is, any chosen radical generates a pair with any other radical in the sample).

For estimation it is necessary to consider the possibility of the forbidden transition in the radical pair [16]:

$$\varphi(r,\theta)=\varphi(r)\text{Sin}^2\theta$$

$$\varphi(r)=2\{3g\beta/(2r^3H_0)\}^2$$

After averaging over all the angles it is possible to obtain:

$$\langle \varphi(r) \rangle = 2(\pi/2)\{3g\beta/(2r^3H_0)\}^2 \sim (D/H_0)^2$$

Where D is a dipole-dipole interaction in a radical pair,  $H_0$  – the main field [17]. Now it is possible to calculate the ratio of the signal in the forbidden field to the signal in the main field. It is necessary for the case of the uniform distribution of the radicals all over the sample. Then the probability to find  $dN$  radicals in a sphere with the radius of  $r \div r+dr$

is equal to:  $dN=n2\pi r^2 dr \sin(\theta) \cdot d\theta$ , where  $n$  is the concentration of the radicals. Let for the simplicity the radicals start to recombine at the distance  $r_o$  and they are uniformly distributed inside the sphere of the radius  $r_a$  (radius of the ampoule). Then the ratio of the EPR signal in the forbidden field to the ratio of the signal in the main field (probability of the transition  $\chi_{1/2}$ ) will be proportional to the value ( first integral is taken from  $r_o$  to  $r_a$ , the second integral is taken from  $0$  to  $\pi$ ):

$$\chi_{1/2}=C*n\int_{r_o}^{r_a} 4\pi r^2 \{3g\beta/(2r^3 H_o)\}^2 dr \int \sin^3 \theta d\theta = Cn(4\pi 9g^2 \beta^2)/(4H_o^2) \int_{r_o}^{r_a} (dr/r^4) =$$

$$=C*n(4\pi g^2 \beta^2)/(H_o^2) \{1/r_a^3 - 1/r_o^3\} = Cn(4\pi g^2 \beta^2)/(H_o^2 r_o^3) \text{ (since } 1/r_o^3 \gg 1/r_a^3)$$

Here  $C$  is the coefficient, that depends upon other parameters. It is possible to see, that the signal itself in the forbidden field should depend upon the concentration as  $n^2$ .

The experiment was performed using the pure nitroxide TEMPOL in X-band (molecular weight 165). His density being considered close to  $1\text{g/cm}^3$  the concentration of the radicals is close to  $n=3.7 \cdot 10^{21} \text{ 1/cm}^3$ ,  $r_o=6.5\text{A}$ . Then

$$\chi_{1/2}=0.0053C$$

Direct measurement shows, that in this case, that is considered as the most clean case of the concentrational radical pairs the ratio of the forbidden signal to the main signal is  $10^{-5}$  and then  $C=0.0019$ .

Now with the help of the formula received it is possible to check the data [14] and to find, that in this case ( $n=2.4 \cdot 10^{19}$  and  $r_0=3.16$  A – the distance between the atoms of Ne in the lattice, at the smaller distances the atoms should recombine) the value  $\chi_{1/2}$  is equal to:

$$\chi_{1/2}=(2.4 \cdot 10^{19}/3.65 \cdot 10^{21})(6.5 \cdot 10^{-8}/3.16 \cdot 10^{-8})^3 10^{-5}=6 \cdot 10^{-7}$$

that is one or two orders of magnitude smaller, then the observed in the experiment ( $\sim 10^{-5}$  [14]). (In reality the atoms can't be placed at such a small distance – in this case the fine structure of the signal of the radical pairs would be easily observed. For more reasonable value of  $r_0=6.26$  A, that is, the double crystal lattice value, the value of  $\chi_{1/2}=7 \cdot 10^{-8}$ ). It means, that in the case of the atoms of hydrogen, as it was later proved for

the case of the atoms of nitrogen [13] through the direct observation of the fine structure) the signal in a forbidden field is not the consequence of the concentrational radical pairs (it is too strong) but rather the consequence of the presence of some radical pairs with some fixed distances, radical pairs of association.

One more confirmation, that the observation in the EPR spectrum of the signal in the forbidden field almost certainly means the presence in the system of the radical pairs of association follows from the facts outlined in publications [18,19]. In [18] the signal of the radical was observed in the main field and the signal in the forbidden field after the irradiation by the  $\gamma$ -source from Co for the case of the amorphous polyethylene, and in [19] the signal of the radical, the signal in the forbidden field and the signals of radical pairs in the main field were observed for the crystalline polyethylene. In both cases the compound is the same and the radical pairs are obviously the same, but in the case of the crystalline polyethylene the linewidth of the signal is smaller and the radical pairs are clearly seen on the tails of the signal from the radical in the main field. The ratio of the signal in the forbidden field to the signal of the radicals in the main field was equal to  $10^{-5}$  and by the estimations 20% of all the radicals obtained are in the state of the radical

pairs. Therefore, it is possible to explain the forbidden signal by the radical pairs of association, that are not visible in the main field on the tails of the signal of the monoradical.

The problem with the explanation of the signals of the radical pairs, outlined in [9-13] is that in many cases the second important property of the radical is excluded from the explanation – the radical is a strong acceptor and should easily generate donor-acceptor bonds, including the bonds with the other radical. An attempt to explain the stabilization of the radical pairs with the help of the simplest idea of a covalent bond between the radicals has two limitations. According to the concept of covalent bond [20] the complete wave function is the production of the coordinate wave function and the spin wave function (the possibility of the separation of the coordinates and spin coordinates is assumed, otherwise it would be necessary to use the Dirac equation [21]). But for ordinary energy well (one minimum) that is generated between two radicals, the radicals being considered in zero approximation as hydrogen-like atoms (what is possible due to the relatively large distance between the radicals compare to the size of the normal bond) the complete wave function should be antisymmetrical in the lowest energy state.

The coordinate wave function is always symmetrical in the lowest state, then the spin wave function should be antisymmetrical, what corresponds to the singlet state. The result is the recombination of the radicals with the production of a new bond. The triplet low state for such a pair of well separated radicals is impossible. This is the first limitation – a strong bond between separated radicals should be singlet.

The idea of lowest triplet state is applicable, for example, to the case of biradical, where this state is not the lowest in energy (there are lower in energy bonds, that create the skeleton of the biradical) or for the molecule of oxygen, where also there are lower in energy levels, what are responsible for the  $\sigma$ -bond. But the lowest level due to the symmetry consideration should be singlet. Then in order to easily reach the temperature population and to observe EPR-signal, the energy separation between the singlet and the triplet should be so small, that the energy of such a bond is not enough to generate the complex, to hold the radicals near each other at a fixed distance. This is the second limitation of a simple approach – if the triplet state thermally accessible (for the case of well separated radicals), the bond is too weak.

For the case of the donor-accepter interaction between the radicals the lowest level is of course the singlet one, but in this case the next level (triplet level) is not dissociative and due to the specificity of the form of the energy well lies close to the singlet one in energy. In this case it is thermally populated. The same electrons, that are responsible for the charge-transfer bond, spend just part of the time in the state complete charge transfer (this lowers the magnetism of the system, according to [6]), while the main time they spend in the radical pairs state, what allows it to be registered by EPR.

There are cases, of course, when the radicals are forming the diamagnetic dimers [22], creating a special type of bond, for example TCNE<sup>-</sup> and other  $\pi$ -radicals, but those radicals are non sterically hindered and most probably the singlet-triplet separation for those dimers is too large to observe EPR-signal. Because the observation of the EPR signal of radical pair demands some constrains onto the stability and hindrance of the radical, such a signal should be considered more as exception, then the rule, contrary to the complex between the radical and the molecule without the free valency, where the shape of the well does not any matter (the free valency is preserved) and that are highly expected for any radical (for example, in [22] no signal of radical pairs was observed, but

all the radicals were generating complexes with nonradical species (“pimers”) easily.

Also, EPR signal of the radical pair is much less expected for the case of two different radicals, since in this case, according to [18], the energy between the singlet and the triplet state should include the energy difference of the SOMOs of initial radicals and thus can be large.

Another explanation of the existence of the radical pairs of association hold by the donor-accepter bond with the lowest state being triplet needs much more advanced quantum mechanics (second approximation of perturbation theory). While the idea of the singlet level being the lowest follows from quantum mechanics (Landau-Lifshitz [20]), this description is the **first approximation** of the perturbation theory. For the large exchange integral it works fine and explains the strong covalent bond. When the triplet and singlet levels are closer **the second approximation** is necessary, which states that in this case the **triplet level goes down**. Loosely this may be described as application of Hund’s second rule [34] for the unusual case of close energy levels – due to the repulsion between electrons (this is not exchange energy!) the level with wider separation between electrons would be a little less in energy, thus sending the triplet level below singlet and

making the lowest level both triplet and bonding. Once the exchange integral is high, the repulsion between electrons does not big matter and the singlet level goes down (classical covalent bond).

#### 4. Complexes with charge transfer between the radical and nonradical molecule.

Because of the presence of SOMO for the free radical with the energy approximately in the middle of the gap, it should generate charge-transfer complexes very easily, playing the part of an electron acceptor in this case (see higher). (A similar explanation of the generation of the bond between the radical and the molecule is outlined in [22]). There is a lot of observations, that demonstrate, that the free electrons are readily generate complexes with charge transfer, in this case the stabilization of the radical itself takes place. This is especially important at the investigation of the biological objects, where because of complexity of the biological molecule the radical has many points of attachment (points of complex generation).

For example, in [23] it was discovered, that relatively unstable ubisemiquinone radical increases its stability for many orders of magnitude, as it forms the charge-transfer complex with some biological molecules (in the case discussed in the article it was

cytochrome bd). In addition, the stabilization of the naphtho-semiquinone radical was investigated in a binding site. Also the semiquinone forms of menaquinone analogs were investigated (menadione and vitamin K<sub>1</sub>). Such a stability is of big importance, since in many intrinsic radical reactions in biology the radical can be stable just due to the complex production (in photosynthetic center, for example). Such a possibility is rarely considered now, but because of strong acceptor properties of the radical it can indeed take place.

In [24] the charge-transfer complexes were considered as responsible for the stabilization of the semiquinone radicals in the cigarette tar. According to the authors opinion, the quinone, the semiquinone radical and the initial pyrochatechol are generating several types of the complexes of the sandwich types, which are responsible for stabilization of the otherwise unstable o-semiquinone radical.

Complexes with charge-transfer can be observed not just through the stabilization of the radical as in [23,24], but also directly by the observation of the appearance of the additional splittings in the EPR-spectrum of the radical in a solution [25]. Due to the generation of the charge-transfer complex between the nitroxide and DMSO

uncompletely resolved additional structure in EPR-spectrum was detected. It was checked, that such splittings disappear for the case of fully deuterated DMSO.

Despite the radical is a strong acceptor, for some complexes between the nitroxide radicals (plays a part of an acceptor at interaction with a donor) and very strong acceptors the complexes of the free radicals can be generated, where the radical is a donor of the electron [26].

#### 5. Complexes of the free radical with the production of hydrogen bond.

This type of complexes between the radical and the nonradical molecule was especially well investigated. However, both GAUSSIAN calculations and many experimental results suggest that the hydrogen bonding always accompanied by charge transfer. For example, in the classical example of quinhydrone complex between the p-quinone and hydroquinone there is charge transfer and two hydrogen bonds.

Nevertheless, hydrogen bonding can be considered as a separate type of the complex, because in many cases the typical hydrogen bonding molecule (water, alcohol) is generating the complex with the radical in a way similar to the hydrogen bonding in a classical sense (like water + water). Another good reason for numerous publications on

that type of complex is that this type of complexes was found for nitroxide radicals which are the most popular object of investigation in EPR. For the case of nitroxide radicals the hydrogen bonding complexes can be calculated using GAUSSIAN program.

Hydrogen bonding complexes may be detected through the observation of the change of hyperfine splitting due to complex generation [27]. In another paper [28] at investigation of the influence of the process of hydrogen bonding with the molecule of the solvent onto the hyperfine splitting of nitroxide by two methods FTIR and EPR it was shown, that it is the hydrogen bond complex that influences mainly the hyperfine structure, not the dielectric constant of the medium (the influence of the polarity of the medium is negligible, the existence of the complexes was verified by IR spectrum).

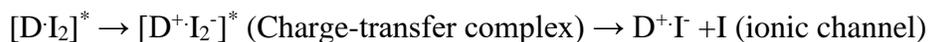
High-field EPR was successfully applied [29] to investigation of the hydrogen bonding complexes between the nitroxide radical and lipid bilayers. It was shown, that HF ENDOR and HF EPR can help to understand the local structure in the vicinity of the nitroxide and to identify the hydrogen bond through the observation of the splitting of  $g_{xx}$  component.

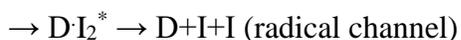
But not just nitroxide radicals generate the complex with other molecule with the help of a hydrogen bond. For example, in [30] by using multifrequency EPR and by comparison of the spectra in the solution and in the solid matrix it was shown, that in the case of the phenoxy radical, captured in the matrix of the appropriate phenol, there is a hydrogen bond formed, what reveal itself as anomaly large hyperfine splitting onto the hydrogen atom. Such splitting is absent in the case of the solution, probably due to the complex instability caused by Brownian motion, and the splitting can't be explained in any other way.

#### 6.Charge-transfer complexes of radicals and the mechanisms of chemical reaction.

Since in real experiments the observation of the short-lived complexes is always a big challenge, this part of the article has mainly a speculative character.

In a famous work in femtosecond chemistry [31] the generation after the exiting pulse of a very short-lived complex with charge transfer was observed, the complex can decay further into the ionic pathway as well as into the radical parthway:





In this reaction the charge-transfer complex plays an unusual role of the unified species, that can switch the mechanism of the chemical reaction from ionic pathway (S<sub>N</sub>2 mechanism) into the radical pathway, just creating the basis for some unified mechanism, where both types of the reactions are parts of some more general approach.

In another publication [32] it was observed the reveal of the so-called roaming mechanism of photodissociation, when two parts of the molecule, both of them are radicals are “roam” around each other before separation into the different directions. Pure speculatively it is possible to suppose, that the force, that holds them together is the coulomb force – there is a production and then the decay of the complex with charge transfer between two radicals – most probably the same mechanism of the coulomb interaction is responsible for the pairing of the atoms at the gas discharge at some large distances from each other, later they would be freezed in the matrix of the noble gas as radical pairs [13-15].

Pure speculatively it is possible to expect the appearance of the short-lived charge-transfer complex as an intermediate in the reactions, where the competition

between  $\text{SN}_2$  mechanism and the reaction of one-electron transfer (radical pathway) is observed (see, for example, [33]) .

### Conclusions.

The donor-accepter bond between radicals and between radical and non-radical molecule should play a big role in chemical interactions and responsible for some unusual phenomena (like radical pairs of associations). This bond was considered in old textbooks together with covalent, ionic, donor-accepter but was omitted in the last years. Despite the free radicals are scarce in biological chemical reactions (due to high reactivity and DNA immediate damage) such chemical bond should not be neglected in the future quantum chemical calculations – it is stronger than van-der-Waals bond but weaker than covalent bond. Similar arguments are applied to hydrogen bonding of free radicals – should be very popular in chemistry but rarely taken into the consideration.

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