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The Electronic Structure of Radical-anions

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The ESR spectroscopic data relating to studies on the chemical and electronic structures of radical-anions derived from organic compounds have been examined. These studies include those on the distribution of unpaired electron density in radical-anions, the effect of substituents on such distribution, the hindered motion of groups and fragments in radical-anions, the effect of the solvent on the distribution of unpaired electron density, and the nature of the association of radical-anions with metal cations. Among problems of the chemical behaviour of radical-anions, electron-exchange reactions between the radical-anions and the initial molecules have been considered.
The bibliography includes 124 references.

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I. INTRODUCTION

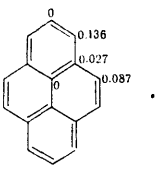
Electron-transfer hypotheses are nowadays widely used to account for the mechanisms of certain chemical reactions. These include the metallation, Wurtz, Grignard, hydrogenation, and certain other reactions [1]. In these reactions radical-anions (RA) are either detected experimentally or are postulated as intermediates. Although the true role of radical-anions in these processes has not been always completely established, their very presence necessitates a careful study of their chemical behaviour.

The application of radiospectroscopic, optical polarographic, quantum-chemical, and other methods yielded extensive data on the physicochemical properties of these species. These techniques have greatly expanded our knowledge of the electronic structure of molecules capable of being reduced with the formation of radical-anions.

The formation of ionic species in the interaction between liquid potassium and naphthalene was noted as early as 1867 by Berthelot [2]. However, systematic studies in this field began with the work of Schlenk [3] in the first quarter of the twentieth century. Schlenk observed that aromatic ketones and hydrocarbons react with alkali metals in ethereal solutions forming coloured free-radical products. The free-radical nature of metal ketyls was confirmed in 1934 by Sugden [4], who showed them to be paramagnetic. In the nineteen-thirties, studies on the reactions of alkali metals with aromatic hydrocarbons were continued by Scott [5], who began the general use of 1,2-dimethoxyethane (DME) as a solvent and demonstrated its exceptional effectiveness in the reaction between aromatic hydrocarbons and alkali metals. A number of studies have been made [6-8] to elucidate the composition of complexes of aromatic hydrocarbons with alkali metals. It has been shown for complexes of anthracene with lithium, sodium, and potassium that, depending on the amount of metal M introduced into the reaction, the composition of the complex with anthracene (A) varies from AM to AM_2. An important property of solutions of these complexes is their high electrical conductivity.

The electronic structure of the products of the reaction of aromatic hydrocarbons with alkali metals has been established by electron spin resonance (ESR) and electronic spectroscopy. Analysis of these data showed that one of the first products of the interaction in solution between aromatic compounds and alkali metals are mono- and di-anions of these compounds linked to some extent to the metal cations. The hyperfine structure (HFS) of the ESR spectra indicates complete transfer of the unpaired electron from the alkali metal to the aromatic hydrocarbon molecule and a high degree of delocalisation of the electron. The simple approximation of the molecular orbital (MO) method is frequently sufficient to describe the nature of the delocalisation of the unpaired electron. Analysis of ESR spectra of numerous hydrocarbon π-electron radicals shows that the magnitude of hyperfine coupling (HFC) to protons (a_H) is proportional to the density of the unpaired electron at the corresponding hydrogen nucleus [9]. Fig. 1 shows the variation of a_H with the unpaired electron density at the carbon atom (ρ_C) in the lowest non-bonding orbital of the radical-anion calculated by the simple MO method. This linear relation constitutes the basis of the familiar McConnell formula [10]: $a_H = Q\rho_C$ ($-Q = 22.5-30$ gauss).

However, there are cases where the simple molecular orbital theory predicts zero unpaired electron densities at carbon atoms, while the ESR spectra show a hyperfine structure due to hydrogen atoms bound to these carbon atoms. As an example, the diagram below shows the distribution of unpaired electron density in the pyrene radical-anion [9,11] based on the simple molecular orbital theory:



The diagram shows that zero unpaired electron densities occur at the terminal protons of pyrene. Nevertheless the ESR spectra of this radical-anion show a hyperfine structure due to these protons with hyperfine coupling constants of 1 gauss.

This discrepancy between the simple molecular theory and the ESR data is due to the fact that the molecular orbital theory yields charge densities of the unpaired

electron, while the hyperfine structure of the ESR spectra is due to the interaction of the unpaired electron spin density (SD) with the paramagnetic nuclei in the radical.

Practical methods for the calculation of spin density in π-electron radicals were proposed by McLachlan [11]. Since a detailed description of the essential features of these methods is outside the scope of this review, we shall only mention that they allow for the interaction of the unpaired electron with the filled π-electron shells. This interaction leads to partial "unpairing" of the electrons with α- and β-spins in filled electron shells, as a result of which they move in orbitals which differ from those predicted by the molecular orbital theory. In this case the spin density at the carbon atom is the sum of the unpaired electron density calculated by the simple molecular orbital theory and the spin densities of electrons corresponding to the α- and β-spins. When the molecular orbital theory yields zero unpaired electron densities, the overall spin density may have a "negative" sign relative to the direction of the spin of the unpaired electron.

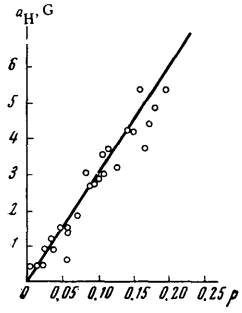


Figure 1. Variation of the proton hyperfine coupling constants in the ESR spectra of the radical-anions of benzene, cyclo-octatetraene, naphthalene, anthracene, naphthacene, pentacene, perylene, coronene, phenanthrene, and biphenyl with unshared electron density at a given carbon atom calculated by the molecular orbital method.

Further studies showed that there exists also a relation between the hyperfine coupling to the carbon-13 and nitrogen-14 nuclei and the distribution of spin density [12]. These relations are more complex but are nevertheless satisfactorily consistent with the concepts of the delocalisation of the unpaired electron in the lowest non-bonding orbital of the radical-anion.

The electronic absorption spectra of anions and dianions may be treated from this standpoint [13-15]. The electronic spectra of these species have characteristic bands in the visible region and the ultraviolet absorption is analogous to that of the initial hydrocarbon. Absorption in the visible region is due to transitions of the unpaired electron in the lowest non-bonding orbital.

An enormous amount of work has been done in the last decade on radical-anions, mostly using the ESR method. One of the most important results of the application of this method in the chemistry of free radicals has been the detection of radical-anions in polarographic reduction carried out directly in an ESR spectrometer [16]. This method, developed by Maki and Geske, greatly extended the possibilities of the synthesis of radical-anions. While reduction with alkali metals is carried out mainly in ethereal solutions, electrochemical reduction allows the use of a larger number of solvents. In many cases it proved possible to employ solvents such as alcohol and water [17], in addition to aprotic solvents such as dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and acetonitrile (AC).

The range of problems solved with the aid of ESR is very wide: the distribution of spin density in various radical-anions, the effect of substituents on the distribution of spin density, the effect of solvent and the hindered rotation of individual groups on hyperfine coupling, electron-exchange reactions, ion association, stability of radical-anions and the way it is influenced by the nature of the metal and the solvent, and chemical reactions involving radical anions.

We decided to isolate only a few main trends in studies on radical-anions without attempting a complete description of the enormous scientific literature which has accumulated recently. One may include here the electronic structure of radical-anions of various classes of chemical compounds, the effect of substituents and medium on the electronic structure of radical-anions, and the formation of ionic association complexes. Among problems related to the chemistry of radical-anions, only electron-exchange reactions will be considered in detail, since extensive and interesting data have accumulated in this field. Until recently there have been no reviews or monographs on this problem in the Soviet literature. Among the reviews published outside the Soviet Union, particular mention should be made of those of Geske [18] and Szwarc [19] and the compilation on radical-ions [20].

II. ELECTRONIC STRUCTURE OF RADICAL-ANIONS

The ESR spectra of the radical-anions derived from an enormous number of organic compounds have now been investigated: polyenes, aromatic compounds with various functional groups, heterocyclic compounds, and organic derivatives of the elements. In describing these extensive experimental data, we decided to separate the most important classes of chemical compounds whose radical-anions have been investigated in detail and also certain trends in this field.

The review of the experimental data should be begun with butadiene as the simplest example. The radical-anion from butadiene was obtained electrochemically in liquid ammonia by Levy and Myers [21]. The ESR spectrum of this radical-ion is presented in Fig. 2 and consists of a quintet of triplets with the following hyperfine proton coupling constants (a_i) in the 1- and 4-positions and 2- and 3-positions: $a_1 = a_4 = 7.617$ gauss and $a_2 = a_3 = 2.791$ gauss.

$$\overset{\cdot}{H_2}\overset{1}{C}=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2.$$

The distribution of spin density is described satisfactorily by the wave function $\Psi_3 = 0.600\,\varphi_1 - 0.371\,\varphi_2 - 0.371\,\varphi_3 + 0.600\,\varphi_4$ obtained by Hückel's simple molecular orbital method. The ratio of the coupling constants is $a_1/a_2 = 2.729$ and that of the spin densities is $\rho_1/\rho_2 = 0.600^2 : 0.371^2 = 2.615$. The distribution of spin density in the butadiene radical-anion is confirmed by the analysis of the spectra of the radical-anions obtained from butadiene derivatives [22]: $(CH_3)_2C=CH-CH=(CH_3)_2$ and $H_2C=C(CH_3)-C(CH_3)=CH_2$.

Numerous studies have been made on the radical-anions of benzene derivatives. These include alkyl, cyano-, carbonyl, nitro-, and also certain organometallic derivatives. The distribution of spin density in some of these radical-anions may be interpreted using the properties of the molecular orbitals of benzene [9]. Six molecular orbitals may be formed from the six $2p_z$ atomic orbitals of carbon: three bonding and three antibonding orbitals.

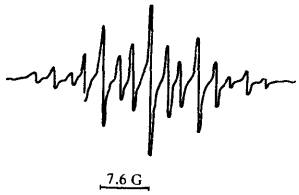
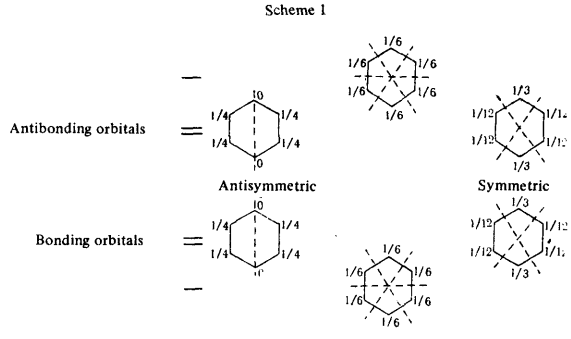


Figure 2. ESR spectrum of the butadiene radical-anion in liquid ammonia at −78°C.

The relative energies of these orbitals and the electron densities are presented in Scheme 1.

Scheme 1



The dashed lines indicate the positions of the nodes of the π-orbitals. The highest bonding and the lowest antibonding orbitals are degenerate. In the benzene radical-anion the unshared electron is equally distributed between two degenerate orbitals. The distribution of the electron in the degenerate orbitals is indicated in the Scheme. These two orbitals may be classified as symmetric and antisymmetric according to their behaviour on reflection in a plane perpendicular to the benzene ring and passing through opposite atoms. The spin density at each carbon atom in the benzene radical-anion is 1/6 and the ESR spectrum consists of 7 lines with binomial intensity ratios and with spacings of 3.75 gauss. [23] In the radical-anions of substituted benzene where the symmetry is less than three-fold the degeneracy is removed. If the perturbation introduced by the substitutent is not too great, then the distribution of the unshared electron proves to be similar to the distribution in one of the degenerate benzene orbitals. The effect of substituents may be examined most simply when the perturbation is purely inductive [9]. If the substituent is electropositive, the unshared electron will occupy the antisymmetric orbital and the ESR spectrum of the radical-anion will consist of a quintet due to the interaction of the unshared electron with the *ortho*- and *meta*-protons with a coupling constant of about 5 gauss. The Scheme shows that the spin density in the antisymmetric antibonding orbital is distributed equally between the four carbon atoms. The hyperfine coupling to the proton in the *para*-position and the nuclei of the substituent should be small.

When the substituent is electronegative, the unshared electron will occupy the symmetric orbital. Here the ESR spectrum will be complex, since it must involve considerable doublet splitting (about 8 gauss) due to the proton in the *para*-position with additional splitting of the doublet components due to the *ortho*- and *meta*-protons. The application of these simple concepts to certain mono- and di-*para*-substituted benzenes gives a good agreement with experiment. Similar concepts were developed for *ortho*- and *meta*-derivatives of benzene [9].

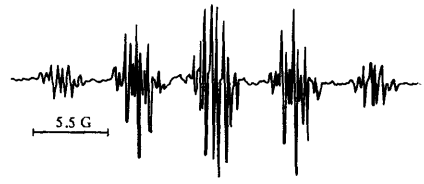
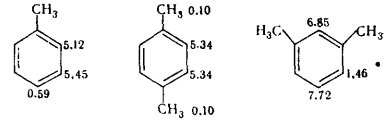
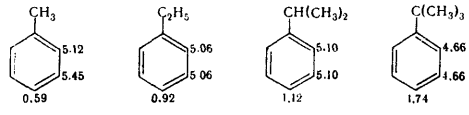


Figure 3. ESR spectrum of the toluene radical-anion in dimethoxyethane containing potassium.

The experimental data on the ESR spectra of the radical-anions of alkylbenzenes clearly illustrate these ideas. Fig. 3 presents as an example the ESR spectrum of the toluene radical-anion. The coupling constants for the toluene and *p*-xylene radical-anions [23–26] indicated in the Scheme below proved to be similar to those predicted by considering the antisymmetric orbital, while in the *m*-xylene radical-anion the distribution of spin density agrees better with the symmetric orbital [24–26]:



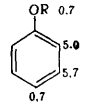
Interesting features are revealed when the ESR spectra of the following radical-anions are compared:



It is seen that, on transition from toluene to t-butylbenzene, there is an appreciable increase of the coupling constant for protons in the *para*-position and a decrease of the constants for the *ortho*- and *meta*-protons [9]. Three causes responsible for this change in the distribution of spin density may be indicated: configuration interaction, vibrational interaction, and thermal equilibrium between two states close to degeneracy. These mechanisms should lead to an admixture of a symmetric wave function with the antisymmetric wave function in the wave function of the unpaired electron. The high value of the coupling constant for the *para*-hydrogen in the radical-anion of t-butylbenzene is regarded as a result of the mixing of two states. The role of the vibrational interaction between the antisymmetric and symmetric states decreases with

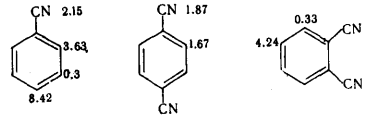
increasing distance between these two states. If the distance between the levels become comparable to kT, thermal population of the highest vacant orbital at room temperature becomes possible. When this condition applies, the coupling constants should depend on temperature. Such a variation has been observed by Tuttle [27] and de Boer and Colpa [28]. The sum of the coupling constants $a_H(para) + a_H(CH_3)$ diminishes as the temperature is lowered, while the sum $a_H(ortho) + a_H(meta)$ increases by the same amount. The hyperfine coupling constants for the *p*-xylene radical-anion are independent of temperature, which may be accounted for by long distances between the levels [28]. Estimates of the distance between the two states yield 384 cm^{-1} for toluene and 868 cm^{-1} for *p*-xylene.

Another example illustrating the effect of electropositive substituents on the degenerate benzene orbitals is the ESR spectra of the radical-anions of alkoxybenzenes investigated by Grandberg et al. [29]:



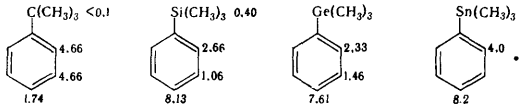
where R = CH_3 or C_2H_5.

The cyano-group has a filled π-bonding and a vacant antibonding orbital the interaction of which with the π-orbitals of benzene must be considered in the analysis of the ESR spectra of the radical-anions of cyanobenzenes. However, here too the concepts developed above are applicable to the analysis of the ESR data for the radical-anions of benzonitrile, terephthalonitrile, and phthalonitrile:



The cyano-group in the radical-anion of benzonitrile and terephthalonitrile lowers the energy of the symmetric orbital and in the radical-anion of phthalonitrile the energy of the antisymmetric orbital is reduced [9].

The concept of the orbital degeneracy of the benzene levels proved useful in the examination of a number of other substituted benzenes [30,31]:



Above it was shown that the unshared electron in the radical-anions of monoalkylbenzenes occupies the antisymmetric orbital. Analysis of the hyperfine structures of the ESR spectra of the radical-anions of benzene derivatives containing silicon, germanium [30], and tin [31] shows that in these radical-anions the symmetric orbital lies below the antisymmetric orbital. The simple concepts developed above permit the classification of these substituents as electronegative. However, one must not disregard certain features in the ESR spectra which may be associated with conjugation. Thus the high values of the hyperfine coupling constants for methyl protons in the radical-anion of trimethylsilylbenzene may reflect the occurrence of some interaction between the vacant *d*-orbitals of silicon and the π-electrons in the benzene ring.

The examples examined illustrate the removal of degeneracy in cases where the unshared electron is located either in the symmetric or the antisymmetric orbital. However, weak perturbation by a substituent may lead to only a slight redistribution of spin density between these orbitals. Such a situation was observed by Fraenkel and coworkers [32] in the radical-anion of monodeuterobenzene in which one hydrogen atom was replaced by deuterium. In contrast to the benzene radical-anion for which a hyperfine coupling constant of 3.75 gauss was found, the following hyperfine coupling constants were obtained for monodeuterobenzene: $a_H^2 = a_H^3 = a_H^5 = a_H^6 = 3.92 \pm 0.01$ gauss, $a_H^4 = 3.41$ gauss, and $a_D^1 = 0.55 \pm 0.01$ gauss. The introduction of deuterium leads to a somewhat greater population of the antisymmetric orbital compared with the symmetric orbital. Köhnlein et al. [33] succeeded in removing the degeneracy in the benzene radical-anion itself by a suitable choice of conditions. The ESR spectrum of the benzene radical-anion in a 2 : 1 tetrahydrofuran (THF)—dimethoxyethane mixture changes on raising the temperature above −20°C—the seven lines with a binomial distribution of intensities are replaced by a main triplet ($a_H^1 = 6.5$ gauss) with further splitting of each triplet component into a quintet ($a_H^2 = 1.75$ gauss). The authors suggest that the removal of degeneracy is due to exchange interaction with the metal cation, as a result of which the unshared electron occupies the symmetric orbital.

Apart from benzene, the radical-anions of a number of compounds with D_{3h}, D_{6h}, and D_{8h} symmetries having degenerate electronic states have been investigated: triphenylene, *sym*-tricyanotriazole [34], *sym*-trimethylsilylbenzene [35], trinitrobenzene [36], coronene [37], and cyclooctatetraene [38]. When the radical-anions of *sym*-tricyanotriazole, *sym*-trimethylsilylbenzene, and trinitrobenzene are generated chemically, the distribution of spin density shows a deviation from the symmetry of the initial molecules. These deviations are attributed to the removal of orbital degeneracy and to the distribution of spin density in each of the degenerate orbitals. The interaction of the metal cation with one of the functional groups is regarded as a possible cause of the removal of degeneracy [36].

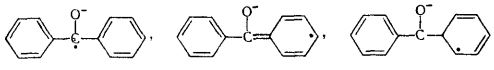
Cyclo-octatetraene (*COT*) readily accepts two electrons and is converted into a dianion. The ESR spectrum of the cyclo-octatetraene radical-anion consists of nine lines with a binomial intensity distribution and a hyperfine coupling constant of 3.2 gauss. [38] It has been suggested that the addition of one electron results in a flattening of cyclo-octatetraene, so that the radical-anion has a planar structure with D_{8h} symmetry. The electronic structure of planar $COT^{\cdot-}$ should exhibit orbital degeneracy. However, the study of the ESR spectrum of the radical-anion of monodeuterated cyclo-octatetraene does not show any signs of the removal of degeneracy [39]. McLachlan [39] explains the absence of such signs by the fact that the vibrations of the C–C bonds, which leads to the extension or compression of the molecule, interact more effectively with the motion of electrons than do other types of vibrations. These interactions lead to the appearance of orbitals corresponding to a fully symmetrical distribution of spin density.

The above concepts proved unsatisfactory in the study of the ESR spectra of the radical-anions of substituted benzenes with substituents having their own π electrons. In these radical-anions the unshared electron orbitals differ markedly from the benzene orbitals and an independent calculation is necessary for the interpretation of the ESR spectra. Such substituents include the carbonyl, nitroso-, nitro-, and certain other complex functional groups. A satisfactory description of the distribution of spin density in the radical-anions of the above compounds may be achieved by the McLachlan method [11] with a suitable choice

of parameters for the Coulombic and exchange integrals (MO parameters).

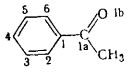
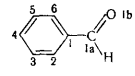
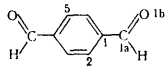
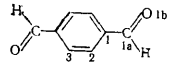
The ESR spectra of *p*-benzosemiquinone [40], *o*-benzosemiquinone [41], 1,4-naphthosemiquinone, 9,10-anthrasemiquinone, *o*-phenanthraquinone, etc. [42] can be satisfactorily described within the framework of the McLachlan method when the following values are adopted for the MO parameters: $\alpha_O = \alpha C + 1.2\beta$ and $\beta CO = 1.56\beta$.

The principal features of the distribution of spin density in the radical-anions of the carbonyl compounds may be examined on the basis of the following valence bond schemes for the benzophenone radical-anion:



from which it follows that in the ESR spectrum of the benzophenone radical-anion there should be a main hyperfine structure due to the protons in the *ortho*- and *para*-position with subsidiary hyperfine structure due to the *meta*-protons. Indeed, Kazakova and Syrkin [43] obtained hyperfine coupling constants of 2.1 gauss for the *ortho*- and *para*-protons and 0.7 gauss for the *meta*-protons.

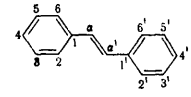
Table 1. Hyperfine coupling constants and spin densities in the radical-anions of carbonyl compounds.

Radical-anion	Position	a_H, G	Spin density (expt.)	Spin density (calc.)
 Acetophenone	1a (CH_3)	6.73	0.2476	0.2540
	1b	—	—	0.1323
	1	—	—	0.090
	2	4.251	0.1794	0.1775
	3	1.070	—0.0451	—0.0554
	4	6.397	0.2784	1.2605
	5	0.875	—0.0369	—0.0446
	6	3.712	0.1566	0.1591
 Benzaldehyde	1a (CHO)	8.507	0.3589	0.3555
	1b	—	—	0.1155
	1	—	—	0.0525
	2	4.685	0.1977	0.1904
	3	1.307	—0.0551	—0.0632
	4	6.471	0.2730	0.2425
	5	0.750	—0.0316	—0.0365
	6	3.393	0.1432	0.1433
 *cis*-Terephthalic aldehyde	1a (CHO)	3.81	0.1607	0.1602
	1b	—	—	0.0871
	1	—	—	0.1434
	2	1.16	0.0489	0.0451
	5	1.54	0.065	0.0641
 *trans*-Terephthalic aldehyde	1a (CHO)	3.89	0.1641	0.1590
	1b	—	—	0.0869
	1	—	—	0.1444
	2	2.08	0.0878	0.0799
	3	0.70	0.0295	0.0298

The ESR spectra of the radical-anions of certain carbonyl compounds show interesting features. A breakdown of the symmetry of the hyperfine interaction relative to the axis passing through the carbonyl carbon atom and the carbon atom in the *para*-position has been observed in the radical-anions of acetophenone, benzaldehyde [44], terephthalic aldehyde [45,46], and 1,4-diacetylbenzene [46]. Table 1 lists the hyperfine coupling constants for the ESR spectra of certain carbonyl radical-anions.

Such non-equivalence of the hyperfine coupling constants for the *ortho*- and *meta*-positions is caused by the interaction of the benzene ring protons with the carbonyl groups. The rotation of the carbonyl group is hindered and its frequency is probably less than the characteristic frequency for relaxation of the ESR spectra (10^7–10^6 Hz). The retardation of the rotation of the carbonyl group results in the existence of *cis*- and *trans*-forms of the radical-anion of terephthalic aldehyde and 1,4-diacetylbenzene [46]. The free energy of the conversion of the *cis*-form into the *trans*-form is $\Delta F_{293^\circ} = -200 \pm 25$ cal mole^{-1} for the terephthalic aldehyde radical-anion and $\Delta F_{293^\circ} = 210 \pm 90$ cal mole^{-1} for the 1,4-diacetylbenzene radical-anion with $N_{cis}/N_{trans} = 1/4$. A satisfactory agreement between the experimental and theoretical spin densities was achieved with the following choice of MO parameters: $\alpha_O = \alpha_C + 1.55\beta$, $\beta CO = 1.5\beta$, and $\beta CC^* = 1.1\beta$, where βCC^* is the exchange integral between the carbonyl carbon atom and the carbon atom in the benzene ring. The asymmetry in the distribution of spin density was achieved by introducing a negative correction to the Coulombic integral for the carbon atom in the 6-position [$\delta = (-0.05)$–(-0.15)].

A similar asymmetry in the hyperfine coupling constant was observed in the ESR spectra of the *trans*-stilbene [47] and *trans*-azobenzene [48] radical-anions:

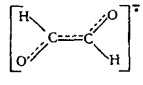


	2	3	4	5	6	α
Stilbene	3.03	0.83	4.00	0.80	1.94	4.51 gauss
Azobenzene	2.81	0.78	2.81	0.78	2.03	4.84 gauss

When account is taken of the interaction between the atoms in the 2- and α-positions and also in the 2′- and α′-positions, which alters the Coulombic integrals for the atoms in the 2- and 2′-positions, it is possible to obtain agreement between the theoretical and experimental spin densities. However, as for the carbonyl radical-anions, the physical significance of this interaction remains unexplained. Maki [45] suggested that the asymmetry may be due to the polarisation of the π-electron cloud by the electrical dipole of the carbonyl group.

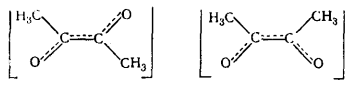
Rieger and Fraenkel [46] described the ESR spectra of a series of radical-anions containing the carbonyl group. These radical-anions are aromatic resonance-stabilised paramagnetic species. However, the less stable aliphatic ketyls, obtained in particular from hexamethylacetone, pentamethylacetone [49], and diethylpinacol [50], have also been investigated.

Recently Russell and coworkers [20] made a large-scale study of the paramagnetic species formed on reduction of conjugated diketones, which have been called semidiones. The reduction of conjugated tri- and tetra-ketones leads to the corresponding radical-anions: semitriones and semitetraones. The simplest representative of semidiones is the radical-anion formed on reduction of glyoxal [51]:



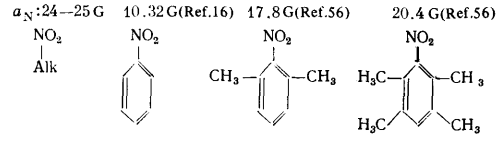
The spectrum of this radical-anion consists of a triplet due to the interaction of the unshared electron with two hydrogen atoms. Analysis of the spectrum permits an estimation of the spin density distribution, according to which the maximum spin density is located at the carbonyl

carbon atoms. ESR spectra revealed the formation of two paramagnetic species in the reduction of diacetyl [52]:



with a signal intensity ratio of 20:1. The study of the temperature variation of these signals made it possible to determine the difference between the stabilities of the isometric semidiones. It was found that the *trans*-isomer is more stable than the *cis*-isomer. The higher values of the hyperfine interaction constants for the *cis*-isomer can be accounted for by the formation of a "more compact" ion pair and the consequent increase of spin density at the carbonyl carbon atoms. The introduction of bulky substituents (isopropyl, t-butyl) leads to the formation of *trans*-isomers only [53]. The study of numerous derivatives of semidiones shows clearly how the hyperfine coupling constants for β-protons depend on the conformation, bond angles, and other factors. These problems will be discussed in greater detail in the next section.

The ease of the electrochemical generation of radical-anions containing the nitro-group permitted a detailed study of the ESR spectra of the radical-anions of a large number of nitro-compounds. The localisation of the unshared electron at the nitro-group is caused by its high electronegativity. The diagrams quoted below show how the structure of the nitro-compounds affects the hyperfine coupling to the nitrogen nucleus in the nitro-group:



where Alk = CH_3, [54] C_2H_5, C_3H_7, or C_4H_9. [55]

While in the radical-anions of aliphatic nitro-compounds the spin density is wholly localised at the nitro-group, in the nitrobenzene radical-anions approximately half the spin density is withdrawn into the benzene ring as a result of conjugation. The decrease of this conjugation caused by the displacement of the nitro-group from the plane of the benzene ring in the radical-anions of *o*-dimethylnitrobenzene and nitrodurene leads to greater localisation of the unshared electron at the nitrogroup as compared with nitrobenzene. Satisfactory agreement between the theoretical spin densities in the radical-anions of nitro-compounds and the experimental values was achieved with the following parameters found by Rieger and Fraenkel [57]: $\alpha_N = \alpha + 2.2\beta$, $\beta_{CN} = 1.2\beta$, $\alpha_O = \alpha + 1.7\beta$, and $\beta_{NO} = 1.67\beta$. The hyperfine coupling constant for the nitrogen atom (a_N) is described by the expression $a_N = A\rho_N^\pi + 2B_0\rho_O^\pi$, where A = 99 ± 10 gauss, $B_0 = -35.8 \pm 5.9$ gauss, and ρ_N^π and ρ_O^π are the spin densities at the nitrogen and oxygen atoms.

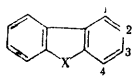
Aliphatic nitro- and polynitro-compounds behave differently on reduction. While mononitroalkanes yield relatively stable primary radical-anions, polynitro-compounds are capable of forming paramagnetic dianions on reduction. Thus in the reduction of tetranitromethane with dithionite in an alkaline medium, Lagercrantz [58] observed the formation of the nitroform radical-dianion $[C(NO_2)_3]^{2-}$. The formation of such a dianion was confirmed by the reduction of the potassium salt of nitroform. The ESR spectrum of the nitroform dianion consists of seven lines with a hyperfine coupling constant for the nitrogen nuclei of 8.4 gauss and intensity ratios corresponding to the interaction of the unshared electron with 3 equivalent nitrogen nuclei. In the reduction of the potassium salt of nitroform the formation of a new radical-dianion $[CH(NO_2)_2]^{2-}$ with the hyperfine coupling constants $a_N = 9.6$ gauss and $a_H = 4.1$ gauss is observed in addition to $[C(NO_2)_3]^{2-}$. The dissociation of the C–C or C–X bonds with formation of the corresponding radical-dianions is observed in the electrochemical reduction of various derivatives of dinitroalkanes [59]. Syrkin and coworkers observed the formation of paramagnetic dianions in the reduction of *p*-dinitrodiphenylmethane [60].

A number of studies have been made on the radical-anions of diaryl systems of the type Ar–Ar and Ar–X–Ar. One of the problems associated with the structure of these compounds is the degree of breakdown of the conjugation between the aromatic rings joined by a single C–C bond. Such breakdown is possible due to the repulsion of the hydrogen atoms and the displacement of the aryl groups from the planes for conjugation. The study of biphenyl [61], 1,1′-binaphthyl [62], and 9,9′-bianthryl [63], in which the angle between the arene planes is ~30°, ~70°, and ~90° respectively, showed that in the biphenyl and binaphthyl radical-anions the unshared electron is delocalised over both aromatic fragments, while in the bianthryl radical-anion it is delocalised over only one fragment.

The study of bridged radical-anions is interesting from the standpoint of the transmission of effects via various –X– groups. The radical-anions of diphenylmethane [64-66], diphenylethane [64-66], phenyl ether [66], *p*-cyclophanes [66,67], di-(*p*-nitrophenyl)methane [68,69], *p*-nitrophenyl ester [68], and di-(*p*-nitrophenyl) sulphide [68] were studied for this purpose. Syrkin and coworkers [65] showed that the initial conclusion [64] that the unshared electron in the radical-anions of diphenylmethane and diphenylethane may be delocalised was based on erroneous experimental data obtained in the measurement of the ESR spectra of secondary radical-anions. The data on *p*-cyclophanes and di-(*p*-nitrophenyl)methane are not unambiguous. The differences in the spectra of the radical-anions obtained from di-(*p*-nitrophenyl)methane are due to the mobility of the hydrogen atoms in the $-CH_2-$ group. Syrkin and coworkers [69] state that, depending on the conditions, it is possible to observe the ESR spectrum of a radical-monoanion in which, according to their data, there is no conjugation, and of the radical-dianion of di-(*p*-nitrophenyl)methane in which the unshared electron is fully delocalised over the entire molecule. An unambiguous conclusion may be arrived at concerning the delocalisation of the unshared electron between the nitro-groups via the $-CF_2-$ group in the radical-anion of difluorodinitromethane on the basis of an analysis of a simple ESR spectrum [70], which consists of a triplet of quintets due to the interaction of the unshared electron with two nitrogen nuclei ($a_N = 12.9$ gauss) and two fluorine nuclei ($a_F = 14.8$ gauss). The delocalisation of the unshared electron was observed in the radical-anion of diphenyl sulphone by Kaiser et al. [71] and also by Gerdil and Lucken [72]. The distribution of spin density in the phenyl rings of this radical-anion is similar to that in the radical-anion of biphenyl.

The intensive studies on the radical-anions of aromatic hydrocarbons and aromatic compounds containing oxygen and nitrogen atoms are largely due to the simplicity of the theoretical analysis of their ESR spectra. The inclusion in the aromatic systems of many-electron atoms such as those of sulphur, phosphorus, and selenium leads to certain difficulties in the interpretation of the spectra. One of the few approaches whereby account can be taken of the effect of these atoms on the electronic structure of organic derivatives of elements of this kind involves the

consideration of the *d* orbitals. The quantum-mechanical method for taking into account the interaction of *d* electrons with *p* electrons proposed by Longuet-Higgins [73] permits the treatment of the sulphur atom as an analogue of the double bond in ethylene. According to Longuet-Higgins, such treatment makes it possible to understand the aromatic nature of thiophen. Since thiophen itself is not reduced, dibenzothiophen and related compounds were chosen to test these hypotheses. The hyperfine coupling constants for protons in benzene rings are presented below [74]:



X	a_1	a_2	a_3	a_4, gauss
O	4.87	0.98	4.87	1.96
S	4.48	0.86	5.16	1.46
Se	4.27	1.02	5.27	1.02
—CH=CH—	0.32	2.88	0.72	3.60.

The calculation of the hyperfine coupling constants within the framework of the Longuet-Higgins scheme, which takes into account the interaction of *p* and *d* electrons, gave the following values for benzothiophen: a_1 = 1.36 gauss; a_2 = 2.30 gauss; a_3 = 0.02 gauss; a_4 = 2.63 gauss (*d* model). At the same time a second calculation was made including the interaction of the π electrons of the aromatic part of the molecule with the lone pair of *p* electrons of sulphur and oxygen. The hyperfine interaction constants obtained agree with experiment better than in the case where account is taken of *d* electrons:

	a_1	a_2	a_3	a_4, gauss
Dibenzothiophen	3.99	—1.23	5.03	0.75 (*p*-model).
Dibenzofuran	4.78	—1.41	4.80	1.86

On the basis of these results, Gerdil and Lucken concluded that the interaction of the *d* orbitals of the sulphur atom with the π orbitals of the aromatic system is slight.

Urberg and Kaiser [20] compared the involvement of various valence states of sulphur in conjugation using as an example thioxanthone and its sulphone. The data show that in both cases the sulphur atom is only weakly involved in conjugation compared with the carbonyl group. Analysis of the ESR spectra of the radical-anions of di-(*p*-nitrophenyl) sulphide, sulphoxide, and sulphone led to the conclusion that the distribution of unshared electron density in these compounds depends little on the valence state of sulphur.

The problem of the d–π conjugation was discussed in the study of the radical-anions of 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole by Strom and Russell [75] and by Solodovnikov and Todres [76]. However, data in favour of d–π interaction were not obtained. This problem also arises in the study of the radical-anions containing a phosphorus atom, such as aromatic and aliphatic phosphines and phosphine oxides [77]. The search for more distinctive effects of the involvement of *d* orbitals in conjugation led to the study of the ESR spectra of non-aromatic radical-anions [78,79] such as $[R_2Si]_n$. The ESR spectra of the radical-anions of the cyclic compounds $[(CH_3)_2Si]_6$ and $[(C_2H_5)_2Si]_6$ provide evidence of the interaction of the unshared electron with six silicon atoms and 12 carbon atoms. This delocalisation is attributed [78] to the interaction of the silicon *d* orbitals, which the authors believe to contain the unshared electron.

III. EFFECT OF SUBSTITUENTS AND THE MEDIUM ON THE ELECTRONIC STRUCTURE OF RADICAL-ANIONS

The review of studies on the effect of substituents, the solvent, and the hindered motion of the functional groups in radical-anions on their ESR spectra requires special consideration. Some of these problems were considered for a number of examples in the preceding section. In particular, it was shown that semiempirical quantum-chemical methods permit a satisfactory description of the effect of substituents on the distribution of spin density. In this section we shall consider certain special methods for the treatment of the effect of substituents.

Rieger and Fraenkel [80] showed that the ratio of the spin densities in the *ortho*- and *para*-positions of the radical-anions is associated with the π energy of the unshared electron:

$$\rho^{\pi}_{ortho}/\rho^{\pi}_{para} = 1/4\,(x_0^2 - 2)^2$$

where x_0 is the root of the secular equation. In the case of a weak interaction between the substituent and the ring $x_0 \to 1$ and the ratio $\rho^{\pi}_{ortho}/\rho^{\pi}_{para}$ approaches 1/4, i.e. the orbital of the unshared electron comes close to the symmetrical benzene orbital. For powerful electron-accepting groups, x_0 tends to zero and the ratio $\rho^{\pi}_{ortho}/\rho^{\pi}_{para}$ tends to unity. For nitrobenzene and the benzonitrile radical-anions, this ratio is 0.83 and 0.43 respectively. Thus the ratio of the spin densities in the *ortho*- and *para*-positions is a quantitative characteristic of the electronegativity of the substituent. However, this method does not seem to be widely used.

Table 2. Nitrogen hyperfine coupling constants and Hammett's σ_p constants for the radical-anions of *p*-substituted nitrobenzenes.

Substituent	a_N, G	σ_p	Substituent	a_N, G	σ_p
NH_2	12.18	—0.172	Br	9.70	0.238
OCH_3	11.57	—0.111	$CONH_2$	8.37	—
CH_3	10.79	—0.129	$COOCH_3$	7.73	0.385
F	10.76	—0.056	CN	7.15	0.674
H	10.32	0.00	$COCH_3$	7.02	0.502
C_2H_5	9.84	—	SO_2CH_3	6.90	—
Cl	9.83	0.238	CHO	5.83	0.50
			NO_2	1.74	0.778

Attempts have been made to take into account the effect of substituents on the hyperfine coupling constants using the Hammett equation. Table 2 lists the hyperfine coupling constants for nitrogen nuclei (a_N) in the radical-anions of *para*-substituted nitrobenzenes [81] and Hammett's σ_p constants (after Van Bekkum [82]).

The analysis of such data carried out by Bowers [20] yielded the following values of ρ in the Hammett equation $\lg(a^X_N/a^H_N) = \rho\sigma_n$ for different solvents: −0.833 in dimethylformamide, 0.888 in dimethyl sulphoxide, and −0.750 in acetonitrile. The correlation between a_N and σ_n is not adequate, but is nevertheless a definite correspondence between these quantities.

Brokskii and coworkers [83,84] found that the relation between a_N and σ_n for the radical-anions of *para*-substituted nitrobiphenyls is described satisfactorily by the equation

$$a^H_N - a^X_N = \Delta a^X_N = 3.60\,\sigma - 0.3$$

where a correlation coefficient $r = 0.958$. Having expressed a_N for the radical-anions of nitrobiphenyls as a function of a'_N for the radical-anions of *p*-nitrobenzene using the results of Maki and Geske [81], these investigators estimated the weakening of the effect of the substituent on a_N when a second benzene ring is introduced:

$$a_N = 5.61 + 0.424\,a'_N,$$

whence it follows that the ratio of the slopes (ρ) of the plots based on the Hammett equations for these two series of compounds is about 0.4. This corresponds to a weakening by a factor of 2.5 of the effect of the substituent in the radical-anions when a second benzene ring is introduced.

Certain examples of the effect of the hindered rotation of functional groups on the ESR spectra of radical-anions were considered in the first section of the review. The asymmetry of the spectra of the carbonyl compounds of azobenzene and stilbene is evidence that there is no free interconversion of the *cis*- and *trans*-forms. These examples relate to "static" cases where the barrier between two conformations is fairly high and the transitions take place at a low frequency and do not affect the ESR spectra. However, there exist examples where in the analysis of ESR spectra it is necessary to take into account the nature of the motion of different groups in the radical-anions. This has been clearly shown by Stone and Maki [85] in the analysis of the hyperfine coupling constants for the radical-anions of nitroalkanes $RR'CHNO_2$. [17,18,85]

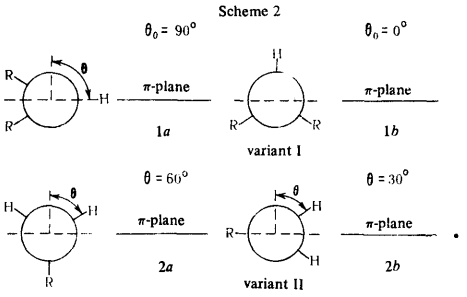
Table 3. Hyperfine coupling constants for the radical-anions of certain nitroalkanes.

R	R′	a_N, G	a_H^β, G	Variant
CH_3	H	25.5	9.75	II
C_2H_5	H	24.8	9.98	II
n-C_3H_7	H	24.2	9.76	II
n-C_5H_{11}	H	25.1	10.1	II
CH_3	CH_3	25.2	4.6	I
C_2H_5	CH_3	24.7	3.19	I
C_2H_5	CH_2OH	24.7	3.26	I

Table 3 shows that the hyperfine coupling constants for the nitrogen nucleus (a_N) are almost independent of the substituents R and R′. In those cases where R′ = H, $a_H^\beta = 9.9 \pm 0.14$ gauss and is independent of R. In radical-anions with one β-proton, a_H^β is much smaller than in the case of two β-protons. The sharp change in the hyperfine coupling constants for the β-proton on transition from RCH_2NO_2 to $RR'CHNO_2$, where R and R′ are alkyl substituents, is attributed to the effect of the hindered rotation of the RR′CH group about the C–N bond. The dependence of the hyperfine coupling constant for β-hydrogen atoms in RR′CH–X on the angle θ is described by the expression $a_H^\beta = Q(\theta)\rho_X^\pi$, [86] where $Q(\theta) = B_0 + B_2\cos^2\theta$, ρ_X^π is the spin density in the $2p_z$-orbital, and θ is the angle between the $2p_z$-orbital and the CH bond projected on a plane perpendicular to the C–X bond. Horsfield et al. [87] determined the constants B_0 and B_2 for the radical $CH_3CHCOOH$ and found them to be 3.2 and 43.5 gauss respectively. Since $B_0 \ll B_2$, it follows that $Q(\theta) \simeq B\cos^2\theta$. In the liquid phase the alkyl groups are not rigidly fixed and Q varies with their rotation. In this case the equation describing the dependence of the hyperfine coupling constants for β-protons on the angle θ must be modified: $a_H^\beta = \langle Q(\theta)\rangle \rho_X^\pi$, where $\langle Q(\theta)\rangle$ is the average value of Q. In the general case $\langle Q(\theta)\rangle$ is the quantum-mechanical average of $\cos^2\theta$ with respect to the rotational wave functions $\Psi(\theta)$. In the limit corresponding to free rotation, $\langle Q(\theta)\rangle = \frac{1}{2}B$ and $a_H^\beta = \frac{1}{2}B\rho_C^\pi$.

It is possible to distinguish several equilibrium conformations (Scheme 2):

Scheme 2



Qualitative examination of these conformations showed that $a_H^\beta(1b) > a_H^\beta(1a)$ and $a_H^\beta(2b) > a_H^\beta(2a)$.

The differences in the hyperfine coupling constants are probably associated with the existence of different equilibrium conformations and with different effects of hindered rotation on $\langle Q(\theta)\rangle$. Averaging in the classical quantum-mechanical approximation leads to qualitatively identical results. An increase in the amplitude of vibrations in the classical case causes a decrease of $\langle Q(\theta)\rangle$ for equilibrium positions in the vicinity of 0° and 30°C and an increase for angles of 60° and 90°. A similar effect causes the barrier height to be reduced in a quantum-mechanical treatment.

Table 4. Splitting constants for the radical-anions of certain organic fluoronitro-compounds.

R	R′	a_N, G	a_F^β, G	Variant
H	F	20.05	28.8	II
CF_3	F	19.25	24.85	II
CF_2OCH_3	F	19.7	49.0	II
CF_2		15.9	93.3	I
CF_2 $CFNO_2$				
CF_2				
CF_3	Cl	21.6	42.1	I

Analysis of the data in Table 3 shows that for variant I $a_H^\beta \neq 0$ and $\theta \neq 90°$, which leads to conformation 1*b*. It follows from the conformations quoted that $a_H^\beta(1b) > a_H^\beta(2a)$, but this is inconsistent with experiment, i.e. it is necessary to suppose that β-protons are not fixed but possess a certain freedom of rotation.

Hindered rotation probably has a significant effect on the hyperfine coupling constants in the ESR spectra of the radical-anions of organic fluoronitro-compounds [88] $RR'CFNO_2$. It may be supposed that the following expression is valid for such anions:

$$a_F^\beta \simeq (B_0 + B\cos^2\theta)\rho_N^\pi + Q_F\rho_F^\pi.$$

For the majority of the radical-anions quoted in Table 4, a_N is constant within the limits of 2 gauss; it is therefore probable that the term $Q_F\rho_F^\pi$ makes a constant contribution to the splitting by β-fluorine atoms in CF_2.

An interesting example of the conformational differences in the structural of the radical-anions of 2,3,5,6-tetraisopropylnitrobenzene was observed by McKinney and Geske [89].

Hyperfine lines corresponding to two different "rotational isomers" A and B appear in the ESR spectrum of this radical-anion. Fig. 4 shows the ESR spectrum which arises when tetraisopropylnitrobenzene is reduced in acetonitrile. The species A and B are characterised by a nitrogen nucleus hyperfine coupling constant of 23.6 and 22.0 gauss respectively. Since the g-factors of A and B are identical, the central components of their spectra merge. The equilibrium constant $K = B/A = 2.3$ and $\Delta G_{298^\circ} = -500 \pm 100$ cal mole^{-1}.

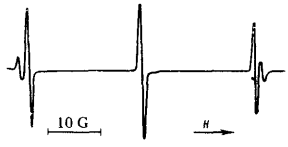


Figure 4. ESR spectrum of the tetraisopropylnitrobenzene radical-anion in acetonitrile.

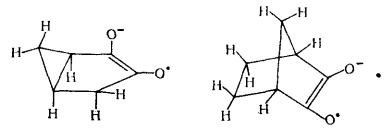
The hindered motion of portions of cyclohexane-1,2-semidione was observed by Lown [90]. At 25°C the ESR spectrum of this radical-anion contains five lines due to the interaction of the unshared electron with four equivalent α-protons ($a_H = 10.34$ gauss is dimethoxyethane). However, on cooling to −96°C, a spectrum consisting of seven lines and corresponding to the two pairs of equivalent protons with $a_H = 14.2$ gauss and $a_H = 6.9$ gauss appears. Hence it follows that a reduction of temperature entails a retardation of inversion and the equatorial and axial protons become distinguishable. At 25°C the inversion frequency is $(14.2 - 6.9) \times 2.8 \times 10.6 = 2 \times 10^7$ Hz, i.e. the lifetime of the radical-anion in one conformation is less than 5×10^{-8} s. Russell and Strom [91] showed that in the ESR spectra of the radical-anions in the series ranging from cycloheptane-1,2-semidione to cyclopentadecane-1,2-semidione at 25°C the signals due to both conformations are present. This is evidence that at this temperature the lifetime of one conformation is $> 10^{-7}$ s.

Talaty and Russell [92] found that the introduction of substituents into cyclohexane-1,2-semidione alters significantly the hyperfine coupling constant for equatorial and axial protons. However, the sum of these constants is virtually invariant (Table 5). These data lead to the conclusion that the observed hyperfine coupling constants (a_{eq} and a_{ax}) are correlated with the true constants ($a^0_{ax} = 13.18$ gauss and $a^0_{eq} = 6.59$ gauss) by the simple equation

$$a_{ax} = 13.18f + 6.69(1 - f),$$
$$a_{eq} = 6.59f + 13.18(1 - f),$$

where f is the fraction of molecules in one of the stable conformations. Calculation with the aid of these equations showed that, with increase in the size of the substituents, an increasing proportion of the molecules are in a stable state and the fraction undergoing ring inversion falls.

Semidiones obtained from bicyclic diketones are of particular interest:



The hyperfine structure of the ESR spectra of these radical-anions contains components due to all the protons present. The assignments of the hyperfine coupling constants are based on a study of the corresponding alkyl-substituted semidiones [20,93,94]. The problems of the mechanism of the transfer of spin density to more remote protons has not been elucidated in detail, but it is suggested that homohyperconjugation takes place in this case.

Table 5. Hyperfine coupling constants (gauss) for 4-substituted cycloalkane-1,2-semidiones at 25°C in dimethyl sulphoxide.

4-Substituent	a_{ax}	a_{eq}	$a_{ax} + a_{eq}$
H	9.83	9.83	19.66
CH_3	12.33	7.34	19.67
$(CH_3)_2CH$	12.63	7.02	19.65
t-Butyl	13.02	6.64	19.66
trans-4,5-$(CH_2)_4$	13.18	6.59	19.77

Analogous effects of the steric positions of atoms on ESR spectra were observed by Russell [20] for semidiones obtained from derivatives of decalin, steroid ketones, bicyclic hydrocarbons, etc.

The hyperfine coupling constants of the radical-anions measured in the ESR spectra refer, strictly speaking, to a definite solvent and depend on its nature. Ludwig et al. [95] observed a change in the hyperfine coupling constant for the nitrogen nucleus in the radical-anion of nitrobenzene from 10.32 gauss in acetonitrile to 9.7 gauss in dimethylformamide. The radical-anions of substituted nitrobenzenes behave similarly [96]. We may note that the changes of the hyperfine coupling constants for protons in the aromatic nucleus are small. However, in the radical-anions of semiquinones the proton hyperfine coupling constants change by 1–45% on transition from dimethyl sulphoxide to aqueous alcoholic solutions [97].

One of the causes responsible for the change in the hyperfine coupling constants is probably a redistribution of spin density in the radical-anions due to the specific solvation of functional groups and the formation of hydrogen bonds. Gendell et al. [98], who suggested the existence of an equilibrium between various types of radical-anion complexes with solvents, succeeded in describing satisfactorily the relation between the hyperfine coupling constants and solution composition. In pure solvents S_A and S_B the complexes R_XS_A and R_XS_B of the radical R_X with one molecule of S_A and S_B exist. In a mixture of solvents there is the equilibrium.

$$R_XS_A + S_B \underset{k_B}{\overset{k_A}{\rightleftarrows}} R_XS_B + S_A$$

It may prove that the hyperfine coupling constant a_A for the nucleus under consideration in the complex R_XS_A differs from the value of a_B for the complex R_XS_B. The observed ESR spectra will depend on the rate of the exchange reaction. For slow exchange, the lifetime of the radical complexes $\tau \gg |\gamma(a_A - a_B)|^{-1}$ (γ is the gyromagnetic ratio for two electrons) and the spectrum will show components referring to both complex R_XS_A and R_XS_B. A case of this kind was observed by Corvaja and Giacometti [99] for the radical-anion of *m*-nitrophenol in water–dimethyl formamide mixtures. In the case of a

rapid exchange, only a single spectrum will be observed with a hyperfine coupling constant having the mean value

$$\tilde{a} = p_A a_A + p_B a_B,$$

where p_A and p_B are the fractions of the complexes R_XS_A and R_XS_B:

$$p_A = \frac{\tau_A}{\tau_A + \tau_B} = \frac{1}{1 + K\alpha}; \qquad p_B = \frac{\tau_B}{\tau_A + \tau_B} = \frac{K\alpha}{1 + K\alpha}.$$

The lifetimes τ_A and τ_B of the complexes R_XS_A and R_XS_B depend on the rate constants and the concentrations:

$$\tau_A = \frac{1}{k_A[S_B]}; \qquad \tau_B = \frac{1}{k_B[S_A]}; \qquad \alpha = \frac{[S_B]}{[S_A]}.$$

The equilibrium constant is

$$K = \frac{k_A}{k_B} = \frac{[R_XS_B][S_A]}{[R_XS_A][S_B]}.$$

The observed mean hyperfine coupling constant $\tilde{a}$ for rapid exchange may be expressed by the somewhat rearranged formula

$$\tilde{a} - {}^1/_2(a_A + a_B) = {}^1/_2[(K\alpha - 1)/(K\alpha + 1)]\Delta,$$

where $\Delta = a_B - a_A$. A plot, based on this equation, of α against $2\delta\tilde{a}/\Delta$, where $2\delta\tilde{a} = 2[\tilde{a} - \frac{1}{2}(a_A + a_B)]$, yields for $K = 10$ the curve in Fig. 5. The value of K was chosen arbitrarily to illustrate the form of the expression [98]. It corresponds to the case where the complex with the solvent S_B is much more stable than the complex with S_A.

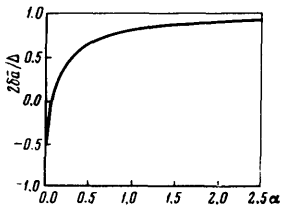


Figure 5. Variation of the hyperfine coupling constant with solvent composition (see text).

The value of $\tilde{a}$ varies rapidly from a_A in the pure solvent to S_A ($\alpha = 0$), since on addition of small amounts of a strongly complexing solvent we have for low values of K a linear relation between $\tilde{a}$ and the hyperfine coupling constants in the pure solvents:

$$\tilde{a} = a_A K\alpha(a_B - a_A).$$

When large amounts of S_B are added, $\tilde{a}$ tends asymptotically to a_B. This type of situation is observed in the variation of the hyperfine coupling constants for the nitrogen nucleus of the nitro-group in the radical-anions of nitrobenzene and *p*-nitroaniline in aqueous acetonitrile mixtures [98]. The addition of small amounts of water leads to an appreciable increase of the hyperfine coupling constant for the nitrogen nucleus. With increase in percentage content of water, this quantity changes little and at a fairly high concentration remains invariant, which is evidence of complete "solvation" of the radical-anion by water molecules.

IV. ION PAIRS

The formation of ion pairs has been investigated hitherto by electrochemical and ultraviolet spectroscopic methods and only recently radioscopic methods began to be used in this field: Symons [100] analysed different ESR spectroscopic data which provide direct or indirect information about the formation of ion pairs in solution: (1) analysis of the dependence of the hyperfine coupling constants on the diamagnetic gegenion; (2) the variation of the properties of the radical-anion, in particular the variation in the symmetry of the spin density distribution; (3) the variation of the ESR line shape; (4) analysis of the ESR spectra of paramagnetic dimers in a triplet state.

We shall consider these data separately. The hyperfine interaction with alkali metal ions is frequently reflected in the ESR spectra of radical-anions in ethereal solutions. This effect was observed by Adam and Weissman [101]. In a study of the ESR spectrum of the sodioketyl of benzophenone they noted the splitting of each component of the spectrum into four lines as a result of the interaction between the unshared electron and the magnetic moment of the ^{23}Na nucleus which has a spin of 3/2. Subsequently such interaction was observed in the ESR spectra of many radical-anions obtained by reduction with alkali metals. In all cases the spin density at the cation is low, but the detection of a small splitting nevertheless permits the conclusion that an ion pair is formed. The data on the hyperfine interaction constants for the nuclei of metal cations (a_M) in various solvents and the calculated spin densities at these nuclei (ρ_{Ns}) are compiled in Table 6 taken from Symons' paper.

It was assumed that $\rho_{Ns} = a_M/a_{atom}$, i.e. the ratio of the hyperfine coupling constants for the metal cation and the free metal in the gas phase. Analysis of the hyperfine coupling constants for the cations shows that the solvent plays a decisive role in the formation of ion pairs. This is associated with the particular solvating capacity of the ions. Unfortunately, this problem has not been investigated adequately on a quantitative basis, and at present one can only note, for example, that the hyperfine coupling constants for the Na^+ cations in the ion pairs with the radical-anions of naphthalene increase on going from dimethoxyethane to tetrahydrofuran and to ethyl ether.

The structure of the radical-anions also plays a significant role. The magnetic interaction depends on the overlapping of the *s* orbital of the cation with the orbital of the unshared electron of the anion. Symons noted that the preferred sites for the localisation of the cation are positions with maximum negative charges.

Atherton and Weissman [102] found an appreciable increase of the hyperfine coupling constant for sodium-23 in sodionaphthalene dissolved in various ethers when the temperature was raised. On lowering the temperature, this quantity tends to zero in tetrahydrofuran solution. The authors suggest that, when the temperature is reduced, the cation is located at the node of the wave function of the unshared electron between the 9- and 10-positions, so that the overlapping of the wave function of the unshared electron in the radical-anion with the *s* orbital of the cation is zero. On raising the temperature, the cation begins to vibrate about its equilibrium position, which leads to an increase of the overlapping and of the hyperfine coupling constants.

Another explanation of this effect is that a decrease of temperature entails an increase of the solvation of the cation and an increase of the distance between the cation and the paramagnetic ion [103]. This type of variation is

regarded as a result of the equilibrium $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$, where A is an ion pair with a hyperfine coupling constant for the sodium nucleus $a_{Na} = 1.5$ gauss and B an ion pair with $a_{Na} = 0$. For higher values of k_1 and k_{-1}, an averaged spectrum will be observed. If two different ion pairs have different hyperfine coupling constants a_A^{Na} and a_B^{Na} and the probabilities of the existence of forms A and B are p_A and p_B, the equilibrium constant K may be expressed in terms of these quantities:

$$K = \frac{p_B}{p_A} = \frac{\tau_B}{\tau_A} = \frac{k_1}{k_{-1}},$$

where τ_A and τ_B are the lifetimes of forms A and B. In the case of rapid exchange between the two forms, a_{Na} will depend on temperature in accordance with the formula

$$a_{Na} = p_A a_A^{Na} + p_B a_B^{Na} = \frac{a_A^{Na} + K a_B^{Na}}{1 + K}.$$

The heats and entropies of reaction have been determined for a number of systems using this expression (Table 7).

Table 6. Cation hyperfine coupling constants (a_M) for ion pairs including paramagnetic anions (M^+A^-).

Anion	Cation	Solvent	a_M, G	ρ_{as}
Naphthalene	Li	THP	0.37	0.26
	Na	THP	1.26	0.40
	Rb	THP	0.09	0.026
	Cs	THP	1.81	0.14
	Na	THF	1.05	0.32
Biphenyl	Li	THP	0.136	0.095
	Na	THP	0.079	0.025
	K	THP	0.083	0.101
	Rb	THP	0.33	0.091
	Cs	THP	1.16	0.142
Anthracene	Li	EE	1.7	0.0
	Na	TMED	2.083	0.66
	K	TMED	0.157	0.19
	Na	MeTHF	1.5	0.47
	Na	MeTHF (-100°)	0.5	0.16
	Na	THP	0.08	0.025
	Cs	THP	0.54	0.066
Azulene	Li	THF	0.174	0.12
	Na	THF	0.538	0.17
	K	THF	0.2	0.24
Pyracene	Na	MeTHF (-80°)	0.176	0.056
	Cs	THF (-100°)	−0.2	−0.024
	Cs	THF (-20°)	−0.7	+0.085
Duroquinone	Li	t-PeOH	0.22	0.15
	Na	t-PeOH	0.85	0.27
p-Benzoquinone	Na	t-BuOH	0.2	0.06
o-Benzoquinone	Li	t-BuOH	0.3	0.21
	Na	t-BuOH	0.2	0.06
Hexamethylacetone	$(Na)_2$	THF (-70°)	1.7	0.54
Benzophenone	Li	DME	0.67	0.47
	$(Li)_2$	DME	1.125	0.79
m-Dinitrobenzene	Na	THF	0.26	0.082
	K	THF	0.2	0.24
	Rb	THF	0.9	0.25
	Cs	THF	2.45	0.30

Note. THP = tetrahydropyran, EE = ethyl ether, TMED = tetramethylethylenediamine, MeTHF = 2-methyltetrahydrofuran, DME = dimethoxyethane, THF = tetrahydrofuran, t-PeOH = t-pentyl alcohol, and t-BuOH = t-butyl alcohol. The temperature of the measurement is indicated in brackets in the second column; in all other cases the experiments were performed at room temperature.

The constants k_1 and k_{-1} and the activation energies for the formation of ion pairs have been determined from the temperature variation of the ESR line widths (Table 8).

Table 7.

	Sodioanthracene in MeTHF	Sodioanthracene in 1:1 THF-MeTHF	Sodionaphthalene in THF	Sodionaphthalene in 1:1 THF-EE
a_A^{Na}, G	1.55	1.55	1.15	1.00
a_B^{Na}, G	0	1.15	0	0
$\Delta H°$, kcal mole^{-1}	−4.6±0.3	−6.2±0.5	−4.8±0.5	−6.4±0.8
$\Delta S°$, e.u.	−23±3	−25±3	−20±4	−33±4

The condition for rapid exchange between ion pairs does not always hold. Thus the ESR spectrum of sodionaphthalene in ethyl ether at low temperatures (below −80°C) corresponds to two different ion pairs with different hyperfine coupling constants for the sodium nucleus: $a_{Na} = 0.8$ gauss and $a_{Na} = 0.06$ gauss. Hirota [103] attributes the higher hyperfine coupling constants to contact ion pairs and the lower values to ion pairs separated by solvent molecules.

Table 8.

	Sodioanthracene in MeTHF	Sodionaphthalene in 1:3 THF-EE
k_1, s^{-1}	$5 \cdot 10^7$ (−60°)	$1 \cdot 10^8$ (−80°)
k_{-1}, s^{-1}	$4 \cdot 10^8$ (−80°)	$7 \cdot 10^8$ (−80°)
ΔE_1, kcal mole^{-1}	3·0	6·0
ΔH_{-1}, kcal mole^{-1}	7.4	11.5

The formation of ion pairs is also reflected in a variation of the hyperfine coupling constants for the radical-anion nuclei as a function of the nature of the cation and the solvent or in relation to the free ion. The free anion is understood to be the paramagnetic species obtained by electrochemical reduction using tetra-alkylammonium salts as a supporting electrolyte. In this case one can neglect the formation of ion pairs with a considerable degree of justification. In some cases, for example, for protons in the 9- and 10-positions of the anthracene anion (the Na^+ and K^+ cations, tetrahydrofuran and tetramethylethylenediamine as solvents) the variation of the hyperfine coupling constant amounts to only a few per cent [100]. In other cases these changes may be much greater. The ESR spectrum of the lithium salt of durosemiquinone in t-pentyl alcohol is characterised by two different hyperfine coupling constants for methyl protons. Thus one may suppose that the lithium cation resides for a relatively long time at one oxygen atom [104]. A similar situation arises in the radical-anion of *m*-dinitrobenzene on formation of an ion pair with the alkali metal cation. As a result of the perturbation introduced by the cation, the hyperfine coupling constant for one nitrogen nucleus is about 10 gauss, while for the other it is about 0.2 gauss. [100]

Interesting information about the kinetic characteristics of ionic association complexes may be obtained by studying the specific broadening of their hyperfine structure lines. We shall examine separately the broadening associated with the change in the hyperfine coupling constants for the alkali metal and radical-anion nuclei. The changes in the hyperfine coupling constants for the metal nuclei may be caused by the reaction [100]

$$(M^+A^-) \rightleftarrows M^+ + A^-,$$
$$(M^+A^-) + M^+ \rightleftarrows M^+ + (A^-M^+),$$
$$(M^+A^-)_1 \rightleftarrows (M^+A^-)_2.$$

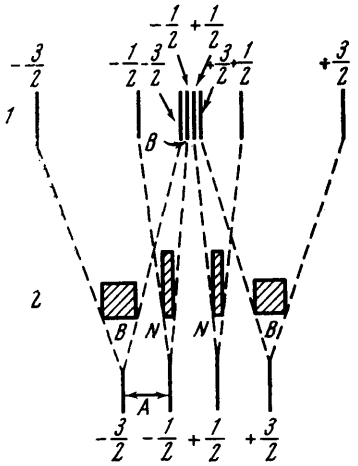


Figure 6. Splitting due to the metal cation ($I = 3/2$) in the ESR spectra of two ion pairs with hyperfine coupling constants A_1 and A_2: 1) slow exchange; 2) intermediate case; 3) rapid exchange.

These reactions affect the lifetime of the paramagnetic species in a definite spin state, which in turn leads to line broadening. The first two reactions cause uniform broadening of all the lines. Hirota and Weissman [105] found that the addition of sodium iodide to the sodioketyl of xanthone leads to an appreciable line broadening. The third reaction represents the conversion of ion pair 1 with a hyperfine coupling constant A_1 into ion pair 2 with a constant A_2. Here the significant factor is that the transition from one type of ion pair to another takes place with participation of one cation. The splitting due to the metal does not disappear in this process. Fig. 6 illustrates the broadening of the lines caused by the third reaction for ion pairs which are in equilibrium and which have metal hyperfine coupling constants a_1 and a_2. [100] In the case of a slow exchange two sets of lines will be observed, as can be seen in Fig. 6 (lines *1*). With increase in the rate of exchange, each pair of lines will become wider until they overlap, and as a result we obtain a single broad line corresponding to each spin state. Since the ±3/2 lines (Fig. 6) are separated in the field considerably more than the ±1/2 lines, the widening of the ±3/2 lines will be much greater compared with the ±1/2 lines (lines *2*). In rapid exchange only a quartet of narrow lines will be observed (lines *3*). Fig. 7 (Hirota [103]) illustrates clearly this type of broadening of the components of the sodium hyperfine structure in sodionaphthalene in a mixed tetrahydrofuran–ethyl ether solvent at different temperatures. It is clearly seen that the two extreme components due to sodium undergo marked broadening at −100°C.

The dynamic nature of solvation is indicated by the specific broadening in the hyperfine structure of the radical-anion itself. It is expressed in an alternation of the hyperfine structure line widths. One of the reasons for the alternation may be the migration of the cation between two equivalent functional groups in the anion. The steady-state pattern associated with this process is determined by the non-equivalence of the hyperfine coupling constants for the nuclei in these functional groups. For example, in the ion pairs of the radical-anions of *m*-dinitrobenzene with alkali metal cations the hyperfine coupling constant for one nitrogen nucleus is 10 gauss and that for the other is 0.2 gauss. [100] Here the situation is complicated by the fact that the same effects can be produced either by the fluctuation of the solvation shell or by conformational transitions in the molecule [106].

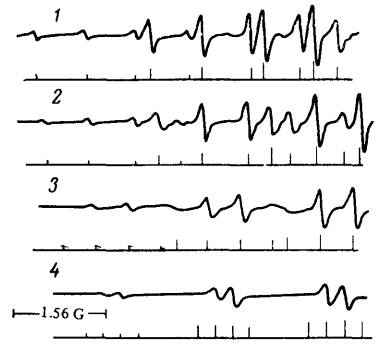


Figure 7. Temperature variation of the line width in the ESR spectrum of the naphthalene radical-anion in the presence of potassium in the mixed solvent tetrahydrofuran (25%)–ethyl ether (75%); the expected relative line intensities in the absence of broadening effects associated with exchange processes are indicated under the spectra: temperature (°C): 1) −60; 2) −75; 3) −85; 4) −95.

Another ionic association process is the formation of paramagnetic dimers observed by Weissman and coworkers [107,108]. A clear example of such structures is the formation of the complexes of the radical-anions of 2,2′-bipyridyl and related ligands with divalent cations (Be^{2+}, Ba^{2+}, and Zn^{2+}). The ESR spectra of these systems in the solid phase at −196°C are characterised by the presence of triplet states corresponding to the structure of the chelate complexes of two radical-anions with a divalent metal cation. The determination of the zero splitting constants from the ESR spectra of the paramagnetic dimers permitted the estimation of the average distance between the anions in the dimers. In the complexes of the radical-anion dimers of 4,7-biphenyl-1,10-phenanthroline, 2,2′-biquinoline, and 2,2′-bipyridyl with the cations Be^{2+}, Mg^{2+}, Zn^{2+}, Ca^{2+}, Ba^{2+}, and Sr^{2+} this distance is approximately 7 Å. [108] The distance between

the radical-anions of hexamethylacetone in the complex with sodium cations is 5.6 Å.[107] Comparison of these distances with the radii of the cations suggests that the dimers have either the structure $A^-M^{2+}A^-$ or $A^-M_2^+A^-$.

V. ELECTRON EXCHANGE REACTIONS

Ward and Weissman[109] observed a pronounced broadening of the hyperfine structure components in the ESR spectrum of the naphthalene radical-anion on addition of free naphthalene to the solution of the radical-anion.

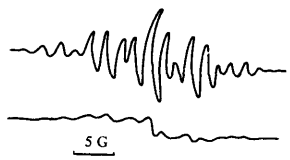


Figure 8. ESR spectrum of the naphthalene radical-anion in the presence of potassium in dimethoxyethane; concentration of radical-anion 1.4×10^{-3} M; upper spectrum recorded in the absence of neutral naphthalene; lower spectrum recorded after the addition of naphthalene to a concentration of 0.218 M.

Fig. 8 presents the original ESR spectra of the naphthalene radical-anions obtained by these investigators before and after the addition of free naphthalene. They attributed this phenomenon to the exchange of an electron between the radical-anion and the naphthalene molecule:

$$C_{10}H_8^{\cdot-} + C_{10}H_8 \rightleftarrows C_{10}H_8 + C_{10}H_8^{\cdot-}.$$

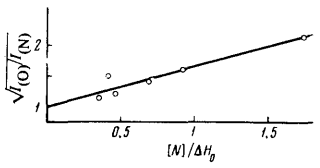


Figure 9. Variation of $I_{(O)}/I_{(N)}$ with $[N]/\Delta H_0$ for naphthalene in the presence of sodium in tetrahydrofuran.

The position of the hyperfine line in the spectrum is determined by the spin quantum numbers of the protons m_α and m_β in the α- and β-positions in the molecule. The transition of an electron from the radical-anion to the neutral molecule alters m_α and m_β to m'_α and m'_β. This process is accompanied by a shift of the resonance line in accordance with the new values m'_α and m'_β. According to Anderson's theory[110], the contribution of such an exchange process to line width is given by the expression $1/\tau = 2\pi\delta\nu$, where $\delta\nu$ is the contribution to line width by the exchange and τ the period between the exchange steps. It is suggested that the line has the Lorentzian shape and the frequency of the exchange is small compared with the difference $\nu_i - \nu_j$ between the frequencies of adjacent hyperfine lines. On the other hand, when $1/\tau > \nu_i - \nu_j$, the exchange results in narrowing of the line.

In practice it proved more convenient to measure not the line width but the intensity, since the two are related:

$$\frac{I_{(N)}}{I_{(O)}} = \left(\frac{\Delta H_0}{\Delta H_0 + \Delta H_N}\right)^2; \quad \sqrt{\frac{I_{(O)}}{I_{(N)}}} = 1 + \frac{\Delta H_N}{\Delta H_0},$$

where $I_{(O)}$ and ΔH_0 are the intensity and line width before the addition of neutral molecules, $I_{(N)}$ is the intensity after the addition, and ΔH_N is the contribution to line width by electron exchange. Simple rearrangement leads to an expression relating k_{exch} (the rate constant for the bimolecular exchange reaction) to line intensity and naphthalene concentration $[N]$:

$$\sqrt{\frac{I_{(O)}}{I_{(N)}}} = 1 + \frac{k_{exch}\,[N]}{\sqrt{3}\pi\, 2.83 \cdot 10^8 \Delta H_0},$$

where ΔH_0 is the width of the ESR line between the points of maximum slope. Fig. 9 shows the variation of $\sqrt{I_{(O)}/I_{(N)}}$ with $N/\Delta H_0$ for sodionaphthalene in tetrahydrofuran. Table 9 lists the exchange rate constants (k_{exch}) in various solvents with different counterions. The data in this Table confirms that the nature of the solvent and the metal have a significant influence on the rate of exchange reactions[109].

Table 9. Rate constants for the exchange between metal-naphthalene and naphthalene.

Cation	Solvent	k_{exch}, litre mole^{-1} s^{-1}
K^+	DME	$(7.6 \pm 3)10^7$
K^+	THF	$(5.7 \pm 1)10^7$
Na^+	DME	$\sim 10^9$
Na^+	THF	$\sim 10^7$
Li^+	THF	$(4.6 \pm 3)10^8$

Further studies by Zandstra and Weissman[111] showed that the rate of the exchange reaction is very different for free ions and ion pairs. Their studies of the reactions

$$C_{10}H_8^{\cdot-} + C_{10}H_8 \rightleftarrows C_{10}H_8 + C_{10}H_8^{\cdot-}, \quad \text{(A)}$$

$$C_{10}H_8^{\cdot-}Na^+ + C_{10}H_8 \rightleftarrows C_{10}H_8 + Na^+C_{10}H_8^{\cdot-}, \quad \text{(B)}$$

in tetrahydrofuran, tetrahydropyran, and 2-methyltetrahydrofuran show that reaction (A) is much faster than reaction (B). Table 10 lists the rate constants and activation energies for these reactions. Remarkable changes in the rate of reaction (B) in tetrahydrofuran are observed when the temperature is reduced. On lowering the temperature below 300°K, the rate of reaction begins to increase and then at 280°K it becomes higher than reaction (A) at the same temperature. To account for this effect, the association of ion pairs with naphthalene is postulated. According to Szwarc[19], the activation energies in Table 10 are too high, the explanation of the anomalous behaviour of the rate constant for the exchange reaction (B) in tetrahydrofuran at a low temperature is not satisfactory, and the effect requires further study.

A similar situation was observed by Hirota [103] in the study of the rates of exchange in sodioanthracene in dimethoxyethane, 2-methyltetrahydrofuran, and in 2-methyltetrahydrofuran–tetrahydrofuran mixtures. To determine the rates of reactions (A) and (B) in the same solvent with the same gegenion, there must be equilibrium between the free ions and ion pairs and the rate of exchange between these species must be sufficiently low to preclude the formation of an average pattern.

Table 10. Rate constants and activation energies for the exchange reaction between sodionaphthalene and naphthalene.

Solvent	Species	Activation energy, kcal mole^{-1}	Temp., °C	$10^{-6}k$, litre mole^{-1} s^{-1}
Tetrahydropyran	ion pairs	17.7±0.9	21	4.4±0.1
	free pairs	18.5±2.2	−23	9.7±4.5
Methyltetrahydrofuran	ion pairs	12.8±3.2	−23	2.8±0.7
	free pairs	12.4±3.6	21	4.5±0.1
Tetrahydrofuran	ion pairs	4.6±0.5	50	34.0±0.8
		−6.8±0.5	−16	71.0±15
	free ions	13.2±1.5	13	38.0±14

Chang and Johnston [112] found that the difference in the rates may be observed with the aid of ESR also when it is impossible to distinguish between the ESR spectra of the ion pairs and free ions. Using the conditions for the so called "rapid exchange" when $1/\tau > \nu_i - \nu_j$ and the exchange leads to the narrowing of the lines, these investigators found a sharp difference in line narrowing in the spectra of free radical-anions and ion pairs. In Fig. 10 the narrow line corresponds to the free radical-anions and the broad line to the ion pairs. The exchange constants obtained from these spectra agree satisfactorily with the data of Zandstra and Weissman [111].

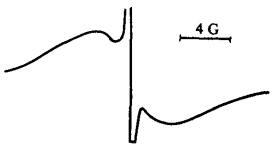


Figure 10. ESR spectrum of the naphthalene radical-anion in the presence of potassium in tetrahydrofuran after the addition of naphthalene to a concentration of 1.4 M.

The study of the rates of exchange in a wider class of compounds showed that molecular structure and the type of interaction between the radical-anion and the solvent have a marked influence on the rate of exchange in different aromatic systems [113]. Table 11 presents data illustrating the effect of the structure of the species undergoing exchange on the electron exchange rate constant.

Adams and coworkers made an interesting comparison of the splitting by nitrogen nuclei in the spectra of the radical-anions of aromatic nitro-compounds and the rates of electron exchange [113]. With increase of the hyperfine coupling constants, there is an appreciable decrease of k_{exch}. This comparison may be followed on the basis of the data in Table 12.

Table 11. k_{exch} in dimethylformamide measured for various aromatic systems.

A/A$^{\cdot-}$ systems undergoing exchange	k_{exch}, litre mole^{-1} s^{-1}
Anthracene	$4.8\cdot10^8$
p-Benzoquinone	$3.8\cdot10^8$
Duroquinone	$6.2\cdot10^7$
1,4-Naphthoquinone	$4.2\cdot10^8$
Nitrobenzene	$3.0\cdot10^7$
Benzonitrile	$2.9\cdot10^8$
m-Nitrobenzonitrile	$1.6\cdot10^8$
Benzophenone	10^8

The same effect on k_{exch} is observed when water is added to dimethylformamide. The increase of a_N on addition of water is accompanied by a decrease of k_{exch}. The data are presented in Table 13.

Table 12. k_{exch} in dimethylformamide for aromatic nitro-compounds.

A/A$^{\cdot-}$ systems undergoing exchange	a_N, G	k_{exch}
Nitrobenzene	9.83	$3.0\cdot10^7$
p-Dinitrobenzene	1.47	$6.0\cdot10^8$
m-Dinitrobenzene	4.68	$5.2\cdot10^8$
p-Chloronitrobenzene	9.18	$7.9\cdot10^7$
m-Chlorodinitrobenzene	8.75	$8.8\cdot10^7$
3,5-Dichloronitrobenzene	7.63	$1.6\cdot10^8$

Interesting details of the mechanism of the electron transfer reactions were obtained by Adam and Weissman [101] in the study of the exchange between the sodium ketyl of benzophenone and benzophenone in dimethoxyethane. Two pathways may be postulated for the exchange reaction:

1. Transfer of an electron from the ion pair to the ketone molecule:

$$Na^+OC(C_6H_5)_2^{\cdot-} + OC(C_6H_5)_2 \rightarrow Na^+ + OC(C_6H_5)_2 + OC(C_6H_5)_2^{\cdot-},$$

$$Na^+ \text{ (free ion in solution)} + OC(C_6H_5)_2^{\cdot-} \rightarrow Na^+OC(C_6H_5)_2^{\cdot-}.$$

2. Transfer of a sodium atom:

$$Na^+OC(C_6H_5)_2^{\cdot-} + OC(C_6H_5)_2 \rightarrow OC(C_6H_5)_2 + Na^+OC(C_6H_5)_2^{\cdot-}.$$

If the reaction takes place via the first pathway, then at high benzophenone concentrations a singlet line should be observed; if the reaction follows the second pathway, a quartet due to the sodium nucleus should be found. The observation of a quartet due to the sodium atom with a hyperfine coupling constant of 1.1 gauss (instead of 1.0 gauss in dilute solution of the benzophenone ketyl) is evidence of the transfer of a sodium atom and of increased spin density at the sodium nucleus as a result of the exchange.

Data on the rates of exchange between different species are of considerable interest:

$$A^{\cdot-} + B \rightarrow B^{\cdot-} + A.$$

The application of ESR yielded only qualitative data, since the rates of such processes are very high and direct kinetic study is extremely difficult [114]. Reactions of this kind were investigated by Arai et al. [115] using pulse radiolysis. The measured rate constants for electron transfer from the biphenyl radical-anion to naphthalene, phenanthrene, *p*-terphenyl, pyrene, and anthracene are very high and lie in the range $(0.26–6.4) \times 10^9$ litre mole^{-1} s^{-1}.

Table 13. Effect of solvation on k_{exch} for exchange between the nitrobenzene radical-anion and nitrobenzene.

Solvent	a_N, G	k_{exch}
DMF–1.6% H_2O	10.17	$9.9 \cdot 10^8$
DMF–4.8% H_2O	10.82	$2.7 \cdot 10^8$
DMF–8.0% H_2O	11.26	$2.7 \cdot 10^8$
DMF–10% H_2O	11.35	$3.2 \cdot 10^8$
DMF–32% ethyl acetate	9.8	$3.1 \cdot 10^7$

From the standpoint of the theory of electron transfer reactions, the comparison of the rate constants for the exchange between A and B (k_{AB}) with the rate constants for the exchange reactions

$$A^{\cdot-} + A \rightarrow A + A^{\cdot-}, \ (k_A)$$
$$B^{\cdot-} + B \rightarrow B^{\cdot-} + B, \ (k_B)$$

is of considerable interest. According to the theory of Marcus [116], there is a definite relation between these quantities:

$$k_{AB} = (k_A \, k_B \, K_{AB} \, f)^{1/2},$$

where K_{AB} is the equilibrium constant for the exchange reaction A and B and $f = 1$ when $K_{AB} = 1$. The applicability of this theory to the electron exchange reaction was tested by Bruning and Weissman [117] on optically pure 1-(naphthyl)-1-phenylethane and the corresponding radical-anion and also the racemic mixture. The first system yields identical rate constants for the exchange between the optical isomers and their radical-anions ($k_d = k_l$) and the second yields rate constants for the exchange between the radical-anion of one isomer and the neutral molecule of the other (k_{dl}): $A_d^{\cdot-} + A_l \rightarrow A_d + A_l^{\cdot-}$.

If the Marcus theory is correct, then $k_d = k_l = k_{dl}$. The rate constants were determined for the potassium salt: $k_d = 0.7 \times 10^8$ litre mole^{-1} s^{-1} and $k_{dl} = 1.1 \times 10^8$ litre mole^{-1} s^{-1} in dimethoxyethane and $k_d = 0.2 \times 10^8$ litre mole^{-1} s^{-1} and $k_{dl} = 0.2 \times 10^8$ litre mole^{-1} s^{-1} in tetrahydrofuran. These data show that the theory, developed largely for electron transfer reactions between variable-valence ions, is indeed applicable to electron transfer reactions between organic compounds.

It is striking that rapid exchange is observed between identical species. Electron exchange is strongly retarded when structural changes are produced by transfer of an electron to a neutral molecule. This is the situation in the radical-anion of cyclo-octatetraene (COT). The experiments of Katz and Strauss [38] showed that after the addition of small amounts of potassium to a solution of 0.7 M COT, a well resolved ESR spectrum of the COT radical-anion is observed. The low rate of exchange between the COT radical-anion and the neutral molecule,

$$COT^{\cdot-} + COT \rightleftarrows COT + COT^{\cdot-}, \quad (1)$$

is due to the fact that the radical-anion has a planar structure, in contrast to the non-planar neutral molecule. Further addition of potassium leads to the obliteration of the hyperfine structure by the reaction

$$COT^{\cdot-} + COT^{=} \rightleftarrows COT^{=} + COT^{\cdot-}. \quad (2)$$

The estimated rate constants for reactions (1) and (2) are about 10^4 litre mole^{-1} s^{-1} and about 10^9 litre mole^{-1} s^{-1} respectively. Since the radical-anion and the dianion of COT have the same planar structure, the rate constants for the exchange between them are much higher than for the exchange between the radical-anion and the neutral molecule [118].

ESR is not the only method for the measurement of rate constants for electron exchange. In many cases the NMR method has been used successfully. The application of NMR is based on the study of the effect of electron exchange on proton line width in NMR spectra. The contribution to the NMR line width (ΔT_2^{-1}) by electron exchange is described by the expression [119]

$$\Delta T_2^{-1} = \frac{f_P \tau_P a^2/4}{1 + f_D \tau_P^2 a^2/4 + 2\tau_P T_{1e}^{-1}},$$

where τ_P and τ_D are the lifetimes in the paramagnetic and diamagnetic states, $\tau_P = 1/k[D]$, $\tau_D = 1/k[P]$, k is the exchange rate constant, $[P]$ and $[D]$ are the concentrations of the molecules in the paramagnetic and diamagnetic states, a is the proton hyperfine coupling constant, f_P and f_D are the fractions of paramagnetic and of diamagnetic molecules, and T_{1e} is the spin–lattice electronic relaxation time. Two limiting cases of slow and rapid exchange are distinguished: slow exchange when $f_D \tau_P^2 a^2/4 \gg 1 + 2\tau_P T_{1e}^{-1}$ and rapid exchange when $f_D \tau_P^2 a^2/4 + 2\tau_P T_{1e}^{-1} \ll 1$. The formulae corresponding to these limiting cases are greatly simplified: for slow exchange $\Delta T_2^{-1} = \tau_D^{-1} = k[P]$ and for rapid exchange $\Delta T_2^{-1} = f_P \tau_P a^2/4 = [P] a^2/4[D]^2 k$. These two limiting cases should differ in the temperature variation of the line width. In the case of slow exchange an increase of temperature should entail a considerable widening of the lines, while in the case of rapid exchange the NMR line should become narrower.

Both these cases were observed by de Boer and McLean [119] in a study of the NMR spectra of *p*-xylene in the presence of the *p*-xylene radical-anions. The lines due to the ring protons became broader on raising the temperature and those due to the methyl protons became narrower. Since the hyperfine coupling constant for the methyl proton is more then ten times higher than for the benzene ring protons in the ESR spectrum of the *p*-xylene radical-anion, the condition of rapid exchange obtained for protons of the first type and the condition of slow exchange obtains for protons of the second type. Studies on the temperature variation of the line width led to the determination of the pre-exponential factor and the activation energy for electron exchange between the *p*-xylene radical-anion and the neutral molecule: $k = 10^{12.0} \exp(-6200/RT)$ litre mole^{-1} s^{-1}.

Williams [120] showed that the rate constants for electron exchange involving the *p*-benzosemiquinone and durosemiquinone radical-anions measured by the NMR method agree satisfactorily with the constants determined by the ESR method.

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One may conclude that considerable progress has been achieved in the study of the electronic and chemical structure of radical-anions. However, at present this progress is to some extent isolated from the development of the chemistry of radical-anions [1,19,121,122]. This is because the reactivity of radical-anions has still been little investigated. Nevertheless a brief survey of the few available data on the reactions of radical-anions leads to the conclusion that factors such as the distribution of the unshared electron [123], association between the anion and cation [124], and the effect of the solvent on the electronic structure and reactions of radical-anions play an important role in their chemistry. Comparison of the kinetic data for electron exchange reactions and reactions involving electron transfer from a radical-anion to a molecule with a different structure are also of considerable interest. The elucidation of the effect of these factors on the kinetic behaviour of radical-anions is undoubtedly one of the essential stages in the study of the role of electron transfer in organic reactions and the extensive data now available on the chemical and electronic structure of radical-anions should in the future make a positive contribution to the solution of this urgent chemical problem.

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