

Zeitschrift: Archives des sciences [1948-1980]
Herausgeber: Société de Physique et d'Histoire Naturelle de Genève
Band: 14 (1961)
Heft: 10: Colloque Ampère

Artikel: Application of the ESR method in chemistry : some new phenomena in electron transfer
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DOI: <https://doi.org/10.5169/seals-739610>

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Application of the ESR method in chemistry

Some new phenomena in electron transfer

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The intensive development of chemistry, especially in the field of high-molecular compounds, biochemistry, and chemical conversions induced by ionizing radiation led to the necessity of broadening the classical concepts concerning complex chemical reactions. The importance of short-lived intermediate substances involving unsaturated bonds, of radicals, was made clear. On the other hand, a great number of chemical investigations show that new molecular properties, accounted for by peculiarities of multi-electron systems and feeble intramolecular interaction, are displayed in reactions involving complex molecules, in catalytic conversions in the condensed phase and in radiation-induced reactions.

An up-to-date physical method successfully used in solving the above problems is that of electron spin resonance. Most important results were obtained by using this method in investigations on free radicals. It appeared possible to obtain very valuable information on the interaction between an unpaired electron and various groups in complex paramagnetic particles as a function of the latter structure.

The present paper will be concerned with ESR investigations on electron transfer and intramolecular interaction in multielectron systems, carried out by the Laboratory of Chemical Radiospectroscopy of the Institute of Chemical Physics in USSR.

1. Explicit studies of negative ions formed by reactions of aromatic compounds with alkali metals in polar solvents were conducted during the last years by Solodovnikov [1]. These ions discovered in 1911 by Schlenk [2] exhibit ESR spectra and are known to be very convenient for quantitative verification of the hyperfine interaction theory [3]. A spectrum of the ion-radical of benzene was obtained. It consisted of seven equally spaced components with binomial distribution of intensities (1:6:15:20:15:6:1). This corresponds to uniform distribution of unpaired electron

densities throughout the benzene ring and to equivalent interaction between the unpaired electron and the six hydrogen atoms of the benzene ring.

A different spectrum was obtained for negative ion-radicals of benzene derivatives of a general formula $(R-C_6H_5)^-$. It consisted of five lines with binomial distribution of intensities. This shows that the unpaired electron interacts with four equivalent hydrogen atoms. It follows from investigation of the structure formula that the unpaired spin is localized mainly in *o*- and *m*-positions of the phenyl ring, while its density in the *p*-position is considerably lower.

It was of interest to find out what will be the unpaired-electron density distribution in ions of the type $Ph(CH_2)_nPh^-$, and to what extent will the bridge of aliphatic CH_2 -groups affect the electron transfer from one phenyl ring to another [1]. It was established experimentally that the spectra of negative ions of diphenylmethane ($n = 1$) and dibenzyl ($n = 2$) consist of 9 main lines with a splitting of 1.9 and 2.5 gauss, respectively. This is about two times lower than the splitting in alkyl derivatives of benzene (~ 4.0 gauss). The appearance of such spectra is due to interaction between the unpaired electron and 8 protons in *o*- and *m*-positions in both phenyl rings. This provides unambiguous evidence that fast exchange of unpaired electrons between the phenyl rings cannot be fully eliminated by the $-CH_2-$ and $-CH_2-CH_2-$ groups, since if the free spin were localized at one ring, the spectrum would obviously consist of five lines. The lower limit on the electron transfer frequency, $\nu_{crit} 10^7$ 1/sec derived from the splitting values for spectra of diphenylmethane and dibenzyl anions can be regarded as a characteristic of the method in this case. At $n = 3$ (for a 1,3-diphenylpropane ion) the exchange frequency is apparently lower than ν_{crit} , and, within the given method limitations, the hydrogen atoms of both rings cannot be considered as equivalent with respect to the unpaired electron. The spectrum obtained consisted of five lines and was similar to that from $(R-Ph)^-$ ions involving electrons localized at one ring. This does not exclude the possibility of electron transfer from one ring to another at a frequency lower than $\nu_{crit} = 10^7$ 1/sec. This could probably be verified by measurements using longer waves.

Another example of electron transfer at a frequency of 10^6 to 10^7 was met with in investigating coals obtained in low-temperature carbonization of sugars. Using a method devised in our laboratory for interpretation of ESR lines by means of plotting linear anamorphoses [4, 5] it was possible to show that transfer of unpaired electrons at a frequency of $\sim 10^7$ 1/sec

occurred in coals. Transfer within one condensed plane polynuclear aromatic system would proceed at considerably higher frequencies. Thus it was natural to suggest that the ν_e values obtained correspond to transfer of unpaired electrons between regions of high conjugation. This may be confirmed by data on ν_e increase in oxygen adsorption. Oxygen acts as a sort of a bridge between two adjacent regions and favours the transfer.

Very interesting information was obtained by Solodovnikov in investigating negative ions of silica substituted derivatives of benzene. A number of investigations led to following conclusions. When a silica atom is attached to the phenyl ring either directly or through a system of conjugated bonds, the unpaired electron density in *o*- and *m*-positions in the aromatic ring is considerably lower than in alkyl substituted derivatives of benzene. Thus for anions of $(CH_3)_3Si-C_6H_5^-$ (I) and $(C_2H_5)_3Si-C_6H_5^-$ (II) ESR spectra consist of five lines of binomial distribution and a splitting of 2.4 gauss (for anions of alkyl substituted derivatives the splitting is 4.0 gauss). The five lines seem to be due to interaction between the unpaired electron and four protons of the ring in the *o*- and *m*-positions. The same is observed for anions of $(CH_3)_3Si-CH=CH-C_6H_5^-$. The only explanation for the narrower hyperfine spacing in these ions would be the shift of the unpaired electron density to silica atoms. Direct evidence for the spin density delocalization involving side groups is the splitting due to methyl protons in the anion of $(CH_3)_3Si-C_6H_4Si(CH_3)_3^-$. Moreover, by using strong magnification it was possible to detect additional weak components in spectra of anions (I) and (II). These are caused by splitting due to the Si_{29} isotope. The shift of the unpaired electron density may be accounted for by the formation of an additional $d_\pi-p_\pi$ bond between the silica and carbon atoms, due to the vacant $3d$ orbitals of silica and the π -electrons in the benzene ring.

The introduction of a methylene chain between the silica atom and the phenyl ring results in a perturbation of the $d_\pi-p_\pi$ conjugation, and the unpaired electron density distribution for these compounds becomes similar to that in alkyl substituted derivatives of benzene.

It will be noted that the conventional methods used before did not permit investigation of delocalization and transfer at a frequency of 10^7 to 10^8 1/sec. These interactions are too weak (10^{-5} to 10^{-6} of a heat quantum) to result in detectable changes in the energy levels of the system. At the same time these frequencies are of the same order as those of elementary chemical acts occurring in complex systems. Consequently,

they may appear to be of great importance in the mechanisms of corresponding conversions.

2. The ESR method makes possible the investigation of energy transfer from one group to another within a molecule, during irradiation. ESR investigations were carried out for compounds of the $A-D$ type (A is a phenyl group and D a hydrocarbon group) [7]. ESR spectra were obtained in radiolysis of frozen compounds of the following classes

- | | |
|--------------------------|-----------------------------|
| (I) $Ph-R$ | $R-CH_3, C_2H_5$ |
| (II) $Ph-(CH_2)_n-SiR_3$ | $R-CH_3, C_2H_5; n=1, 2, 3$ |
| (III) $Ph-C_6H_4-R$ | $R-CH_3, C_2H_5$ |

The radiation-induced yields for all compounds investigated appeared to be lower than the values calculated in accordance with the additivity rule. A spectrum similar to that obtained from irradiated frozen benzene was exhibited in radiolysis of compounds of type I and II. It was established before that the radiation-induced radical yields are by one—two orders lower for aromatic compounds than for saturated hydrocarbons [7]. Thus the appearance of such a spectrum may be considered as direct proof of very effective energy transfer from the hydrocarbon substituent to the aromatic ring. Once the radical yields for aromatic and non-aromatic compounds are known, a quantitative estimate of the probability of energy transfer in a complex molecule of the $A-D$ type may be made. Calculations show that the probabilities of energy transfer for various compounds are within 65-95 per cent. No systematic dependance of the values for probabilities of energy transfer (α) for the compounds investigated on structure could be observed. There seems to be a certain tendency towards decrease in α with longer chains of substituents.

Lines corresponding to broken bonds in substituents appear in the radiolysis of compounds of type PhC_6H_4-R with sufficiently heavy alkyl groups R . However, it may be shown that effective energy transfer to the diphenyl group will occur in this case as well. The thing is, that due to increased stability against radiation of the diphenyl group compared with the benzene group ($G_{R(C_6H_6)} = 0.2$, $G_{R[(C_6H_5)_2]} = 0.03$), there is a marked decrease in broken bonds at the aromatic end of the molecule, while the probable amount of broken $C-H$ bonds in the R substituent will not change considerably with replacement of C_6H_5 by $C_6H_5-C_6H_4$. Thus the relative contribution from alkyl radicals will appear to be consid-

erably increased, though the overall radical yield will be lower than for *Ph-R* compounds.

It follows from the above results that for all compounds investigated electron transfer occurs from *D* to *A* and the probability of it is fairly high.

The transfer of excitation energy through systems involving saturated bonds, made clear by the above discussion, seems to touch upon a field much beyond the scope of radiation chemistry. Indeed, the same mechanism may appear to be valid for chemical reactions in the condensed phase, under the assumption that the migrating energy is not imparted from outside, but liberated in elementary chemical acts and transferred to sufficiently great distances without dissipating as heat. Concepts of this kind were discussed in the papers by Semenov [8] and Semenov and Voevodsky [9].

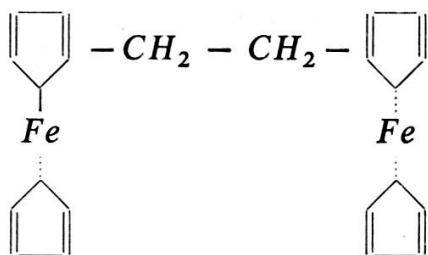
3. All investigations on delocalization and transfer discussed above were dealing with signal carriers of a well known nature. However, certain complex systems, when investigated, displayed paramagnetism that could not be associated with definite paramagnetic centres. This effect was observed for compounds involving sufficiently developed systems of conjugated bonds. « Unpairity » in the ground state of the system was found to occur in many cases and a narrow ESR line of 2 to 6 gauss width appeared. ESR signals from valence-saturated molecules were first observed in 1956 by Kozyrev for linear hydrocarbons involving a continuous chain of conjugated bonds of the polyene type [10]. Later on ESR signals were observed for cyanine dyes [11] and polyphenylacetylene polymers [12, 13]. The *g*-factor of all these signals was practically the same as that of the free spin. The absence of HFS, the small width of the ESR line and its lorentzian form are evidence for considerable delocalization of unpaired electrons. The electron concentrations amounted to 1 electron per 1000 to 10.000 and 10 to 1000 molecules for cyanine dyes and polymers, respectively. The intensity of ESR lines increased with decreasing temperature, obeying the Curie law or slightly deviating from it. The bulk of information permits discarding thermal excitation of the whole molecule to the triplet state, as a possible explanation for the effect. No physical explanation was found so far. The results obtained and observation of ESR lines from these compounds in solution seem to warrant the suggestion that in the case of conjugated double bonds the appearance of unpaired electrons causing narrow ESR signals is related to some unknown properties of such molecular systems. If so, the observed narrow ESR signals from

coals of various origin might be accounted for by «unpairity» in the π -electron cloud of a complex system of conjugated aromatic rings, instead of being the result of broken chemical bonds [14]. Certain indirect evidence for this would be provided by data obtained in investigating oxygen adsorption on sugar coke [14]. It was established that the adsorption of one oxygen molecule diminishes the number of effective signals approximately by 60. This fact, as well as the ready desorption of the oxygen upon degassing seem to be unambiguous evidence that stable chemical bonds are not formed in adsorption. The decrease in intensity of the signal is apparently due to the abovementioned magnetic properties of conjugated-bond systems observed in oxygen adsorption.

These new concepts concerning electron properties exhibited in complex systems of conjugated bonds are of great interest, as they seem to provide a new means of approach to investigations on properties of complex organic compounds.

Other compounds involving conjugated bonds were also investigated in our laboratory, and the majority of these showed ESR signals. It was established, for instance, that magnesium phtalocyanine and phtalocyanine involving no metal exhibit very intensive ESR lines of 1.9 and 5 gauss, respectively. The estimated intensity of the signal shows that the unpaired electron density is one electron to several hundred molecules. In both cases ESR signals disappeared upon dissolution of phtalocyanine in sulfuric acid. *

Similar signals were obtained in our laboratory in investigating ferrocene polymers [15]. The ferrocene dimer



gave no ESR signals.

A polymer of molecular weight 1000 (the chain consisting of about four monomer links) shows an ESR signal of 6.4 gauss width. The line intensity is 10^{17} 1/gr, or one electron for about 10,000 links. The signal disappears when the polymer is dissolved in benzene. A polymer of a molecular

weight of ~ 2000 exhibits a similar signal, which persists, however, in the benzene solution.

Thus all the facts observed are undoubtedly in favour of the suggestion that the appearance of unpaired spins showing a narrow ESR signal is a strictly molecular effect accounted for solely by the conjugation of these bonds and by extensive exchange. When the conjugation is sufficiently strong, as with the ferrocene polymer of a molecular weight 2000, the effect will persist in the solution as well. Whereas for polymers of a lower molecular weight and for phtalocyanines conjugation within the molecule alone is insufficient. An important part is played here by intermolecular exchange that will not occur in solution and, consequently, there will be no ESR signal.

Thus the delocalization of electrons at frequencies of 10^6 to 10^7 1/sec, the transfer of energy through a system of conjugated bonds and the occurrence of paramagnetism in conjugated molecular systems actually seem to show that the ESR method open up entirely new possibilities for investigating feeble interactions that may be of great importance in chemical conversions in the condensed phase. Further work in this field should be in the direction of ESR studies of other possible transfer processes and more explicit investigations on the exchange and delocalization effects on rates and paths of chemical reactions.

* After this paper was presented, information was reported [16, 17] that provides confirmation for the authors' ideas on the nature of the ESR signal from phtalocyanine. It was shown that ESR signals are due not to admixtures, but to peculiarities of molecular and intermolecular structures of phtalocyanines. Of especial interest is the fact [17] that the ESR signal from phtalocyanine is shown by the α -crystalline modification only.