Radicals: Their Molecular Orbitals, Properties, and Reactivity

Petr Čársky and Rudolf Zahradník*

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 12138 Prague 2, Czechoslovakia*

> The experimental evidence ... forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl, $(C_6H_5)_3C$.
>
> H. Gomberg[1]

In this way the existence of the first stable free radical was reported at the beginning of this century. Since that time many thousands of relevant papers have been published on both stable and unstable free radicals. Some of them contributed to progress in applied chemistry (e.g., in macromolecular chemistry); others had great impact on both experimental and theoretical chemistry. An outstanding example of the latter is electron spin resonance (ESR). Besides its chemical applications to specific detection of radicals and to the determination of their structures, ESR was also—indirectly—of great importance to the theory of the chemical bond: it was found that the one-electron wave functions, called Hückel molecular orbitals, give a rather good (sometimes almost quantitative) account of the distribution of the unpaired electron along the skeleton of a conjugated radical. In spite of this, the Hückel method has often been called "naive". The example just noted is not exceptional. As a matter of fact, many typical properties of radicals can be elucidated by rather simple quantum chemical tools.

The definition of radicals has not yet been fixed in the literature. For example, Herzberg[2] defines radicals as short-lived species. According to his definition C_2, C_3, CHF, and HNO are radicals, though they have singlet ground states. In contrast, stable species as NO and ClO_2 with an odd number of electrons are not considered to be radicals. We adopt the definition of Forrester[3] et al.: "A free radical is an atom, molecule or complex which contains one or more unpaired electrons". Although this definition originates from a book in the field of organic chemistry, it is compatible with the quantum chemical notion of "open-shell systems". However, the latter has usually broader meaning because systems in the triplet state (diagram h in Figure 1), atoms with an odd number of electrons, and transition-metal complexes, e.g., $Co^{2+}(H_2O)_6$ and $Fe(CN)_6^{3-}$, are not considered by chemists to be radicals. Furthermore the term radical is sometimes used, in our opinion incorrectly, instead of "substituent" or "functional group".

The diagrams of orbital levels in the ground states of radicals and in the excited states of closed-shell systems are seen, from Figure 1, to have some common features. This is reflected in physical properties and reactivity[4] as indicated in Table I.

In recent years the literature on radicals has been enriched by relevant reviews and publications (e.g., ref 3, 5–9), but a comprehensive review of the applications of MO theory in radical chemistry is still lacking. The available reviews are devoted to selected subjects (e.g., ESR[10] or electronic spectroscopy[8]).

Our aim in this Account is to show how much information can be obtained from basic quantum chemical concepts and routine semiempirical calculations. The second point we emphasize throughout is the comparison of radicals with related closed-shell molecules having one electron more or less. The respective differences in chemical and physical behavior are rather dramatic and in many cases can be treated nicely by MO methods. The open-shell MO treatments may be of use in various branches of chemistry. In Table II we present some selected processes where open-shell systems are involved as transient species.

MO Calculations with Open-Shell Systems

The open-shell theory is typical of a large variety of computational methods. The literature up to 1962 relevant to this topic was reviewed by Berthier.[11] We attempted[9] to supplement this review for the literature up to 1972. Here we restrict ourselves only to two practical remarks:

(a) For those who are going to start their own semiempirical open-shell calculations, the use of the approximate SCF method of Longuet-Higgins and Pople[12] is profitable. In its general form the method is called the half-electron method,[13–15] and its virtue is that one can

Rudolf Zahradník studied at the Technical University in Prague for the C.Sc. degree (equivalent to the Ph.D.). In 1961 he joined the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences and became head of the applied quantum chemistry group. He obtained his D.Sc. in 1967, and in the same year was appointed Associate Professor at Charles University in Prague. Dr. Zahradník's research interests include theoretical interpretations of chemical reactivity, electronic spectroscopy, weak intermolecular interactions, and catalysis.

Petr Čársky received his RNDr. degree from Charles University in 1964. He then joined Dr. Zahradník's group at the Czechoslovak Academy of Sciences, and received his C.Sc. in 1968. His research interests center on chemical applications of molecular orbital theory.

(1) H. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900).

(2) G. Herzberg, "The Spectra and Structures of Simple Free Radicals", Cornell University Press, Ithaca, N.Y., 1971, p 2.

(3) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals", Academic Press, London, 1968.

(4) R. Zahradník and S. Beran, *J. Catal.*, submitted for publication.

(5) E. T. Kaiser and L. Kevan, Ed., "Radical Ions", Interscience, New York, N.Y., 1968.

(6) J. K. Kochi, Ed., "Free Radicals", Vol. 1 and 2, Wiley, New York, N.Y., 1973.

(7) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, Amsterdam, 1967.

(8) P. Čársky and R. Zahradník, *Top. Curr. Chem.*, **43**, 1 (1973).

(9) R. Zahradník and P. Čársky, *Prog. Phys. Org. Chem.*, **10**, 327 (1973).

(10) E. G. Janzen, *Acc. Chem. Res.*, **2**, 279 (1969); see also I. A. Abronin and G. M. Zhidomirov, *Teor. Eksp. Khim.*, **8**, 589 (1972).

(11) G. Berthier in "Molecular Orbitals in Chemistry, Physics, and Biology", P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N.Y., 1964, p 57.

(12) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68**, 591 (1955).

Table I
Common Features of Radical Ions and Lowest Excited States of Closed Shell Molecules[a,3]

Radical cation	Lowest electronically excited state	Radical anion
High EA (easy reducibility)	High EA (easy reducibility) Low IP (easy oxidizability)	Low IP (easy oxidizability)
← Low-energy transition in the electronic spectrum →		
← Numerous electronic transitions in visible, or even in the near-ir region →		
← Lower binding energy in comparison to the parent molecule →		
Prolongation of some bonds[b]	Prolongation of almost all bonds	Prolongation of some bonds[b]
High reactivity toward nucleophiles	High reactivity toward both nucleophiles and electrophiles	High reactivity toward electrophiles
Paramagnetism	In the case of triplet states paramagnetism	Paramagnetism
← Different state symmetry from the parent system →		
Different spin multiplicity from the parent system	In the case of triplet excited states different spin multiplicity from the parent system	Different spin multiplicity from the parent system

[a] Abbreviations: EA, electron affinity; IP, ionization potential; ir, infrared. [b] In general, the prolongation concerns different bonds in cations and anions.

Table II
Formation of Radical Ions by Processes of Different Types

Radical cations	Radical anions
Noncatalytic processes	
1. Action of oxidizing agents (e.g., Lewis acids)	1. Action of reducing agents (e.g., alkali metals)
2. Electrochemical oxidation	2. Electrochemical reduction
3. Electron impact (mass spectrometry)	3. Capture of thermal electrons
4. Uv and γ irradiation	4. Uv and γ irradiation
Catalytic processes	
1. Semiconductor of p type: depletive chemisorption	1. Semiconductor of n type: depletive chemisorption
2. Semiconductor of n type: cumulative chemisorption	2. Semiconductor of p type: cumulative chemisorption

Figure 1. Typical diagrams of orbital levels for open-shell systems: (a–c) radicals; (d) biradical; (e) triplet ground state; (f) radical cation; (g) radical anion; (h) excited state of a closed-shell molecule.

use any program for closed-shell molecules by making two small modifications[15] in the expressions for the density matrix and the total electronic energy. We performed[16,17] an extensive comparison of PPP and CNDO results given by the half-electron method and the "true" SCF open-shell procedure of Roothaan.[18] In all cases we found that the two methods give very similar results. The use of the half-electron method is profitable for certain types of electronic configurations for which the Roothaan method diverges.[17,19] The half-electron method may also be used easily for configuration interaction calculations covering singly excited states since expressions are available for the matrix elements[9,20] that are well adapted for computer programming.

(b) It should be kept in mind that the relationships currently used with closed-shell systems (e.g., the expressions for ionization and transition energies) do not hold for radicals and cannot be applied automatically to the latter. Actually, their forms depend on the SCF procedure used.

Physical Properties

Geometries. Nowadays very efficient procedures are available for geometry optimizations. These are based on the variable metric method, and their application to radicals is straightforward. The inherent constituent of these methods is the evaluation of the energy gradient. In SCF–MO–LCAO treatments, the evaluation of the energy gradient requires the analytical evaluation of derivatives of integrals over the basis functions with respect to all nuclear coordinates. In the semiempirical treatments of the CNDO and INDO types only overlap and two-center electronic repulsion integrals are to be differentiated. Since the necessary derivatives for these integrals are expressible in closed analytic forms,[21] the computer programs are now available for routine closed-shell calculations. The program by Pančíř also permits performance of open-shell calculations and determination of the least energy path,[22] i.e., the reaction coordinate. To illustrate the utility of the program we present the results of our study on the cyclopropenyl radical.[23] The calculations were of the CNDO/2 type, and the half-electron method was used. It has been found that the highly symmetric form (D_{3h}) is subject to the Jahn–Teller distortion, giving the prolate distorted structure I (C_{2v}) which is stabilized by 7 kJ/mol in comparison to the oblate structure II (C_{2v}). The hypothetical D_{3h} structure is about 43 kJ/mol higher in energy than I. Moreover, it has been shown that II corresponds to the saddle point on the reaction coordinate which represents the migration of the short C–C bond of form I:

(13) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968).

(14) M. J. S. Dewar and N. Trinajstić, *Chem. Commun.*, 646 (1970).

(15) F. O. Ellison and F. M. Matheu, *Chem. Phys. Lett.*, **10**, 332 (1971).

(16) P. Čársky and R. Zahradník, *Collect. Czech. Chem. Commun.*, **36**, 961 (1971).

(17) P. Čársky and R. Zahradník, *Theor. Chim. Acta*, **26**, 171 (1972).

(18) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

(19) D. H. Sleeman, *Theor. Chim. Acta*, **11**, 135 (1968).

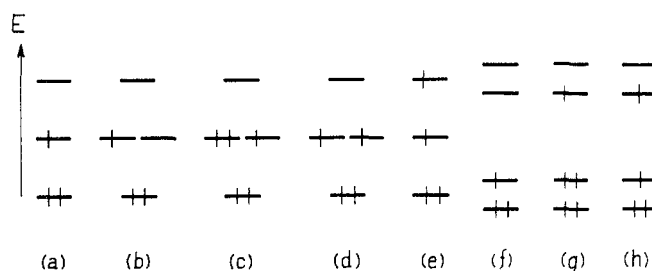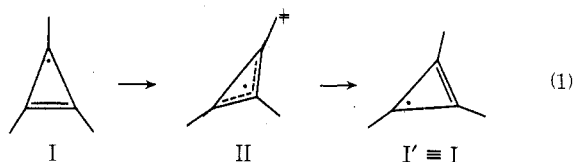(20) A. Ishitani and S. Nagakura, *Theor. Chim. Acta*, **4**, 236 (1966).

(21) J. Pančíř, *Theor. Chim. Acta*, **29**, 21 (1973).

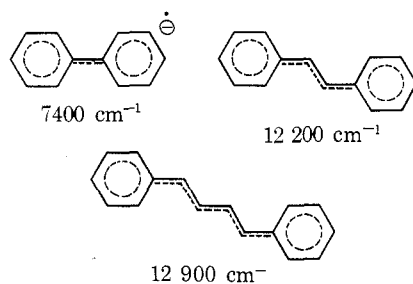(22) J. Pančíř, *Collect. Czech. Chem. Commun.*, **40**, 1112 (1975).

(23) J. Pančíř and R. Zahradník, *Tetrahedron*, submitted for publication.

(1)

    I   II   I' ≡ I

Structure and Absorption (Color) of Radicals. As regards the position of the longest wavelength bands, the neutral radicals resemble the related closed-shell cations and anions. Radical ions present a completely different situation. Here electron uptake to or electron withdrawal from the parent closed-shell system brings about a large red shift of the first band; the larger the shift, the shorter the wavelength of the absorption of the parent closed-shell system. This empirical finding can be easily interpreted for conjugated systems by means of the Hückel MO theory.[24] The gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital determines the position of the longest wavelength band for the majority of conjugated compounds. Typically, this gap is much larger than the gap between the two highest occupied or two lowest unoccupied orbitals, where the lowest energy electronic transition of radical ions is to be expected. This effect is more pronounced than the effect of favorable configuration interaction in some alternant hydrocarbons which brings about that the longest wavelength band (α band) is due to the second transition. Thus, in going from the parent closed-shell molecule to its radical ion the red shift may be as large as 50 000 cm^{-1}, and in many cases the longest wavelength band is located in the near-infrared region (Figure 2). Experimentally, this region is not always easily accessible and consequently, in many cases, the first observed band corresponds to a transition to the second excited state. Since the origin of the lowest energy transitions in radical ions is different from that in the parent closed-shell molecules, there is no reason to expect the same trend for the dependence of the transition energies on structure. To illustrate this we note on the electronic spectra in the series of α,ω-diphenylpolyenes. With the parent hydrocarbons the following transition energies of the longest wavelength bands were found:

40 500 cm^{-1}

32 500 cm^{-1}

25 800 cm^{-}
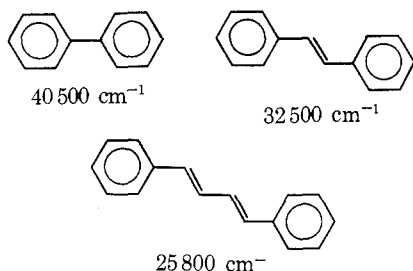
But with the radical anions the transition energies are as follows:

7400 cm^{-1}
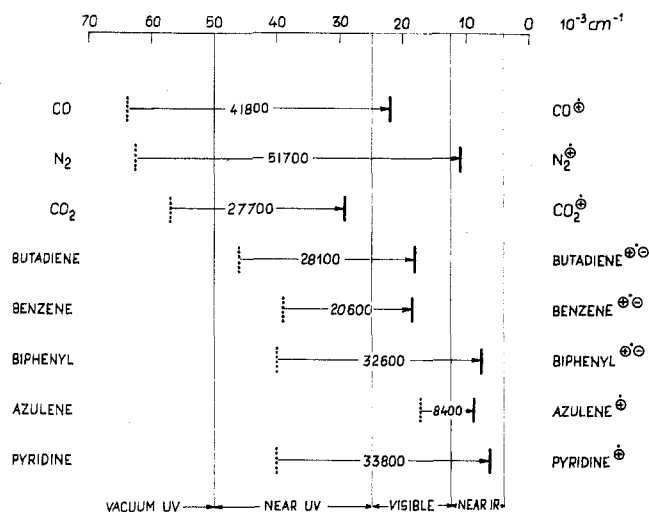
12 200 cm^{-1}

12 900 cm^{-}

Figure 2. Positions of the first absorption bands of a few molecules (dotted lines) and of the radical ions (full lines) thereof. The shifts in the positions of the first bands are indicated by arrows.

Valuable information on the position of excited doublet states can be inferred from the photoelectron spectral data:[25] the energy gaps between the first and the other peaks correspond to $D_0 \rightarrow D_n$ transition energies. Determination of these transition energies is straightforward, and the data inferred in this way are in good agreement with SCF–CI calculations. Nevertheless, in comparing photoelectron spectral data with the direct spectral measurements it must be kept in mind that the former are measured in the gas phase and the latter mostly in solution. Quantitative quantum chemical treatments of electronic spectra of radicals were reviewed by us recently.[9] Attention has been paid to spectra of radicals of the allyl and benzyl type,[26] of radical ions derived from benzenoid[24,27,28] and nonalternant hydrocarbons,[29-31] and of semiquinones,[32,33] and to spectra of radical ions derived from heterocyclic systems.[34,35]

We have also studied the electronic spectra of small radicals[36,37] and radicals having degenerate ground states.[38-40] We found that the CNDO level of approximation is not suitable for these types of radicals. In

(24) R. Zahradník and P. Čársky, *J. Phys. Chem.*, **74**, 1240 (970).

(25) R. Zahradník, P. Čársky, and Z. Slanina, *Collect. Czech. Chem. Commun.*, **38**, 1886 (1973).

(26) P. Čársky and R. Zahradník, *J. Phys. Chem.*, **74**, 1249 (1970).

(27) G. H. Hoijtink, N. H. Velthorst, and P. J. Zandstra, *Mol. Phys.*, **3**, 533 (1960).

(28) P. Čársky and R. Zahradník, *Collect. Czech. Chem. Commun.*, **35**, 892 (1970).

(29) P. Čársky, O. Chalvet, S. Hünig, D. Scheutzow, and R. Zahradník, *Collect. Czech. Chem. Commun.*, **36**, 560 (1971).

(30) I. Nykl, V. Rejholec, P. Hobza, P. Čársky, R. Zahradník, and K. Hafner, *Collect. Czech. Chem. Commun.*, **34**, 1463 (1973).

(31) I. Nykl, A. Fojtík, P. Hobza, P. Čársky, R. Zahradník, and T. Shida, *Collect. Czech. Chem Commun.*, **38**, 1459 (1973).

(32) P. Čársky, P. Hobza, and R. Zahradník, *Collect. Czech. Chem. Commun.*, **36**, 1291 (1971).

(33) P. Hobza, P. Čársky, and R. Zahradník, *Collect. Czech. Chem. Commun.*, **38**, 641 (1973).

(34) R. Zahradnik, P. Čársky, S. Hünig, G. Kiesslich, and D. Scheutzow, *Int. J. Sulfur Chem.*, *Part C*, **6**, 109 (1971).

(35) S. Hünig, D. Scheutzow, P. Čársky, and R. Zahradník, *J. Phys. Chem.*, **75**, 335 (1971).

(36) R. Zahradník and P. Čársky, *Theor. Chim. Acta*, **27**, 121 (1972).

(37) P. Čársky, M. Macháček, and R. Zahradník, *Collect. Czech. Chem. Commun.*, **38**, 3067 (1973).

(38) J. Kuhn, P. Čársky, and R. Zahradník, *Theor. Chim. Acta*, **33**, 263 (1974).

(39) J. Kuhn, P. Čársky, and R. Zahradník, *Collect. Czech. Chem. Commun.*, **39**, 2175 (1974).

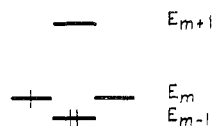(40) P. Čársky, J. Kuhn, and R. Zahradník, *J. Mol. Spectrosc.*, **55**, 120 (1975).

Figure 3. Typical electronic configuration for which a quartet state may be the lowest excited state.

many cases, several states correspond to one electronic configuration and the respective calculated energies differ by terms containing integrals such as, e.g., $K_{\sigma,\pi}$ or $K_{\pi,\pi'}$. As the latter vanish in the CNDO approximation, the observed energy splittings can be reproduced only if a more advanced approach (e.g., INDO) is used. For example, the $(3\sigma)(1\pi)^2$ configuration of CH gives rise to $^4\Sigma^-$, $^2\Delta$, $^2\Sigma^-$, and $^2\Sigma^+$ states. The CNDO–CI calculation predicts for all these states the same energy of 29 100 cm^{-1}, whereas the INDO–CI calculation[40] gives 6300, 25 300, 32 300, and 34 300 cm^{-1}, respectively. With larger systems a smaller energy splitting is to be expected. Nevertheless, for the molecule as large as the diacetylene cation the energy differences are still significant: the $^4\Pi_u$, $^2\Pi_u$ (1), $^2\Phi_u$, and $^2\Pi_u$ (2) states which arise from the $(1\pi_g)^2(2\pi_u)$ configuration are predicted[40] by INDO–CI to lie 16 300, 19 400, 22 300 and 27 100 cm^{-1} above the $X^2\Pi_g$ ground state, in contrast to CNDO which gives a single value of 19 600 cm^{-1}.

With the naphthalene anion radical we augmented the CI treatment for doubly excited states.[41] Their effect on the predicted spectral data was found to be unimportant. Among the other relevant papers we note the studies on radical anions of nitro compounds,[42] various conjugated systems (CNDO/S),[43] and substituted benzyl radicals.[44] In the study[45] of derivatives and hetero analogs of conjugated hydrocarbons the solvent effect was explicitly accounted for in the Hamiltonian.

Lowest Quartet States. In almost all radicals with a doublet ground state the lowest quartet state is located above one or several of the excited doublet states. This is in contrast to molecules with an even number of electrons, where the triplet state is the lowest excited state and sometimes even the ground state. A somewhat striking location of the lowest quartet state is due to the fact that the low-energy electron promotions involve the singly occupied orbital and can therefore give rise only to doublet states. If the electron promotion occurs from a doubly occupied orbital to an unoccupied orbital, the electronic configuration with three singly occupied orbitals is formed. Such a configuration gives rise to two doublet and one quartet states. In accordance with Hund's rule it holds that the $D \rightarrow Q$ energy is lower than the $D \rightarrow D$ energy. In Figure 3 we present a special case of the orbital level diagram for which the quartet state may be the lowest excited state. If we adopt a simple one-electron approach, a simple condition may be formulated for a quartet state to be the lowest excited state, viz., that for orbital energies the relationship $(E_m - E_{m-1}) < (E_{m+1} - E_m)$ must obtain (cf. Figure 3). Experimentally it was established[46,47] that quartets are the lowest excited states in O_2^+ and NH$^+$.

Figure 4. Temperature dependence of the equilibrium constant given by ab initio SCF calculations.[50] The experimental value is indicated by the full circle.

Reactivity

In principle, the reactivity of radicals can be treated quantum chemically in the same way as the reactivity of closed-shell molecules. If a rate process is to be examined, the most advanced theoretical approach consists of the two following steps. The first is the computation of the energy surface by accurate ab initio calculations beyond the Hartree–Fock limit. To give an example of such a treatment we cite the study of the H + F$_2$ → HF + F process.[48,49] The second step is the classical trajectories calculation. The theoretical treatment of this type involves extensive calculations and is therefore feasible only for the simplest systems. With equilibrium processes the situation is more favorable. For a quantitative estimate of the equilibrium constant by means of a statistical thermodynamic treatment, it is sufficient to determine the molecular geometries and to calculate molecular energies and force constants for all reaction components. In Figure 4 we present the result of such an ab initio treatment[50] of the Li + H$_2$O $\rightleftharpoons$ LiOH + H reaction. Perfect agreement between theory and experiment is in this case most likely due to the cancelation of basis set and correlation effects. Below we comment on the semiempirical treatments and on equilibrium aspects of dimerization and disproportionation of radicals.

Dimerization. We attempted to arrive at the quantitative estimates of equilibrium constants of radical dimerizations by means of semiempirical calculations. The calculations were met with a varying degree of success. MINDO/2 calculations were in a fair agreement with experiment for the coupling reactions of CH$_3$, NH$_2$, and HCO.[51] Satisfactory results were also obtained[52] for NF$_2$ which was treated by a modified CNDO/2 method. In contrast, MINDO/2 treatments of NO, NO$_2$, and CN failed badly. From this it may be concluded that existing semiempirical methods are not capable of providing reliable estimates of the heats of radical dimerizations.

Another type of dimerization occurs with radical ions. Here a complex is formed which consists of one molecule of the radical ion and one molecule of the parent

(41) P. Čársky and R. Zahradník, *Theor. Chim. Acta*, **17**, 316 (1970).

(42) T. Shida and S. Iwata, *J. Phys. Chem.*, **75**, 2591 (1971).

(43) H. M. Chang, H. H. Jaffé, and C. A. Masmanidis, *J. Phys. Chem.*, **79**, 1118 (1975).

(44) E. Gey and N. E. Kruglyak, *Z. Phys. Chem. (Leipzig)*, **256**, 737 (1975).

(45) S. Miertuš and O. Kysel, *J. Phys. Chem.*, submitted for publication.
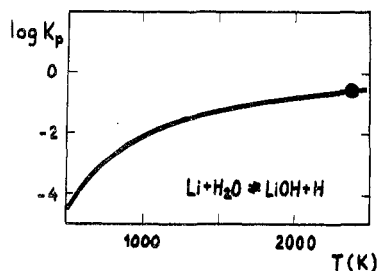
(46) A. B. F. Duncan, "Rydberg Series in Atoms and Molecules", Academic Press, New York, N.Y., 1971.

(47) R. Colin and A. E. Douglas, *Can. J. Phys.*, **46**, 61 (1968).

(48) S. V. O'Neil, P. K. Pearson, and H. F. Schaefer III, *J. Chem. Phys.*, **58**, 1126 (1973).

(49) C. F. Bender, C. W. Bauschlicher, Jr., and H. F. Schaefer III, *J. Chem. Phys.*, **60**, 3707 (1974).

(50) P. Čársky, R. Zahradník, and I. Kozák, *Chem. Phys. Lett.*, **41**, 165 (1976).

(51) R. Zahradník, Z. Slanina, and P. Čársky, *Collect. Czech. Chem. Commun.*, **39**, 63 (1974).

(52) Z. Slanina, J. Schlanger, and R. Zahradník, *Collect. Czech. Chem. Commun.*, in press.

closed-shell molecule. Cation dimers are more abundant, presumably because of the circumstances that the systems studied were rather donors than acceptors. Apparently, the binding energy in a dimeric ion radical is due to a charge transfer. The charge transfer is also recognizable in the electronic spectra of dimeric ion radicals. With the butadiene dimer radical cation, our CNDO calculations led to the correct interpretation[53] of the long-wave absorption which was previously assigned erroneously to the monomeric butadiene radical cation. Recently, a similar study was reported on the ab initio level for ethylene.[54]

Disproportionation. We recognize the following types of radical disproportionations

$$2A\cdot \rightleftarrows R^+ + R^- \qquad (2)$$

$$2A\cdot^+ \rightleftarrows R^{2+} + R \qquad (3)$$

$$2A\cdot^- \rightleftarrows R^{2-} + R \qquad (4)$$
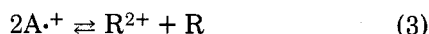
The heats of reaction for processes 2–4 may be treated by means of the MO theory in a very simple way.[55] The three oxidation levels in any of these processes differ merely by the occupation of the highest occupied orbital. If the lower orbitals are taken as a "core" and the energy of the unpaired electron in the radical is ϵ_m, then the energy of the oxidized form is zero and the energy of the reduced form is $2\epsilon_m + J_{mm}$. The reduced form is disfavored by the repulsion between two electrons that occupy the highest orbital, φ_m. A quantitative measure for this repulsion is the Coulomb repulsion integral

$$J_{mm} = \int\int \varphi_m(1)\varphi_m(2)\frac{e^2}{r_{12}}\varphi_m(1)\varphi_m(2)\,d\tau_1 d\tau_2 \qquad (5)$$

which may be related to the energy change in disproportionation. Obviously, a method like HMO which disregards electronic repulsion gives $\Delta E = 0$ for all disproportionations. Since J_{mm} is always positive, in the gas phase, the equilibria 2–4 should always favor the radicals. With conjugated radicals having 4–22 p_z orbitals, J_{mm} ranges from 3 to 7 eV depending on the size and the structure of the radical (and, of course, on the parameter set used in the semiempirical calculations). Figure 5 shows that this simple approach may be useful for estimates of the stability of radicals within one class of related systems. Empirically it was found that radicals with $J_{mm} > 4$ eV do not disproportionate in polar aprotic solvents.[55] If $J_{mm} < 3.5$ eV they disproportionate easily. From the published data it is possible to estimate the change of the enthalpy of solvation in disproportion to 3–5 eV, which corresponds just to the "critical" J_{mm} values. Since J_{mm} is roughly proportional to the size of the conjugated system, a simple rule may
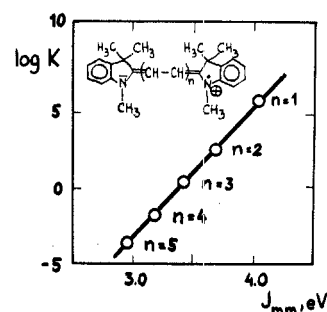

Figure 5. Plot of the logarithms of disproportionation constants against the coulomb repulsion integrals for a series of 1,3,3-trimethylindolenin violenes.[56]

be formulated, viz., that radicals that undergo disproportionation easily do not tend to dimerize, and vice versa (see also ref 57).

Reaction Coordinate. For several radical reactions we investigated the behavior of reactants along the approximate least energy path on the energy hypersurface. Among the possible ways of ethylene oxide formation, a CNDO and MINDO study[58] suggested an important role for the $O_2\cdot^- + CH_2{=}CH_2$ reaction, in which the anionic perepoxide radical formed initially decomposes into C_2H_4O and O^-. An analogous reaction with propene results in stable products of the perepoxide type which may change into propene oxide or propene peroxide. Systematic investigation was devoted to the reaction coordinates for decomposition of cyclopropane radical ions and cyclopropyl radical to various one-, two-, and three-carbon products.[59]

Miscellaneous Reactions. A correlation was found between the observed pK_a values of protonated nitrobenzene radicals with the EHT energy changes.[60] The electronic structures of a group of established and potential biological oxidizing agents (including radicals and radical ions) were investigated by the INDO method. Their oxidizing power was given in terms of gas-phase electron affinities. Conversion of O_2 to H_2O_2 and especially the thermodynamics of early changes of O_2, under physiological conditions, were analyzed ($O_2 + e \rightarrow O_2\cdot^-$; $O_2\cdot^- + H^+ \rightarrow HO_2$).[61] The stability of oxygen-containing radicals increases dramatically in the presence of transition elements;[62] the electronic structure of the respective complexes is under study.[63] Finally, the isomerization reaction of the C_2H_2N radical was analyzed by means of semiempirical calculations; the cyclic form appears to be considerably more stable than the open form.[64]

(57) M. J. Gibian and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973).

(58) S. Beran, P. Jírů, B. Wichterlová, and R. Zahradník, *Catal., Proc. Int. Congr., 6th, 1976*, in press.

(59) S. Beran and R. Zahradník, *Collect. Czech. Chem. Commun.*, in press.

(60) P. Čársky, A. Fojtík, and R. Zahradník, *Collect. Czech. Chem. Commun.*, **37**, 2515 (1972).

(61) P. Hobza and R. Zahradník, *J. Theor. Biol.*, submitted for publication.

(62) A. Tkáč, K. Veselý, L. Omelka, and R. Přikryl, *Collect. Czech. Chem. Commun.*, **40**, 117 (1975).

(63) P. Pelikán, A. Tkáč, and R. Zahradník, unpublished results.

(64) Z. Slanina, Z. R. Grabowski, and R. Zahradník, in preparation.

(53) P. Čársky and R. Zahradník, *Theor. Chim. Acta*, **20**, 343 (1971).

(54) J. Almlöf, A. Lund, and K.-Å. Thuomas, *Chem. Phys. Lett.*, **32**, 190 (1975).

(55) P. Čársky, S. Hünig, D. Scheutzow, and R. Zahradník, *Tetrahedron*, **25**, 4781 (1969).

(56) F. Linhart, Dissertation, Würzburg, 1970.