Quantitative Frontier Orbital Theory. Part 3.† Radical Reactions

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The method of calculatng *ab initio* charge distributions in frontier orbitals, previously described, is applied to some reactions involving radicals. The differential hydrogen abstraction from propionic acid by methyl and chlorine radicals is explained. For radical substrates the method is not applicable, since the orbital approximation is untenable, but it is shown that unpaired spin charge densities, calculated from UHF wavefunctions, give satisfactory correlations with the site of reaction.

In previous publications [1,2] it was shown how the Dean and Richards sphere-charge technique,[3] extended to evaluate partial charges in single orbitals as well as total charge distributions, could be used to rationalise the selectivity observed in aromatic electrophilic substitution [1] and ring closure reactions.[2] The site of attack correlates with the total charge density for ' hard ' (*i.e.* charged and highly polarising) species and with the frontier orbital charge density for ' soft ' species. In the latter case, the method has the advantage over the traditional frontier orbital approach [4] that the nodal properties of the orbital in question are taken into account, which is not the case when coefficients are used.

The principle of the method is simple; integration of the square of the wavefunction is carried out within the limits of the required sphere. The computational difficulties in this procedure are surmounted by a matrix transformation which allows the co-ordinate origin to be set at the centre of the sphere. This can be repeated as many times as necessary in a single calculation, giving a set of localised charges whose accuracy corresponds with that of the starting molecular wavefunction. We have found it convenient to use wavefunctions of *ab initio* quality, but for applications to larger molecules the use of semi-empirical methods would be quite feasible.

Uncharged radicals are invariably ' soft ' entities; for radical attack on a substrate molecule, therefore, one is interested in the frontier charge distribution. In the simple MO picture a radical has a singly occupied molecular orbital (SOMO) which can interact profitably with both the HOMO and the LUMO of the substrate. Which interaction is more important will depend on whether the radical is ' electrophilic ' (relatively low energy SOMO; substrate HOMO more important) or ' nucleophilic ' (relatively high energy SOMO; substrate LUMO more important). Using these ideas the classic example of hydrogen abstraction from propionic acid has been studied.

The HOMO and LUMO charges in spheres surrounding the hydrogen atoms of propionic acid, as calculated by the Dean and Richards method, are shown in Figure 1. In each case the sphere has a radius of 0.54 Å (half the carbon–hydrogen internuclear distance). *Ab initio* molecular wavefunctions were employed, obtained from the GAUSSIAN/76 program [5] with an STO-3G basis set.[6] An experimentally determined geometry [7] for the propionic acid was used. In order to obtain values for the LUMO an occupation number of 2 was assigned in the molecular orbital calculation while leaving the analytical form of the orbital unchanged. We call the quantity obtained the ' capacity of electron acceptance ' of the LUMO. It has been shown [2] that this is a justifiable procedure.

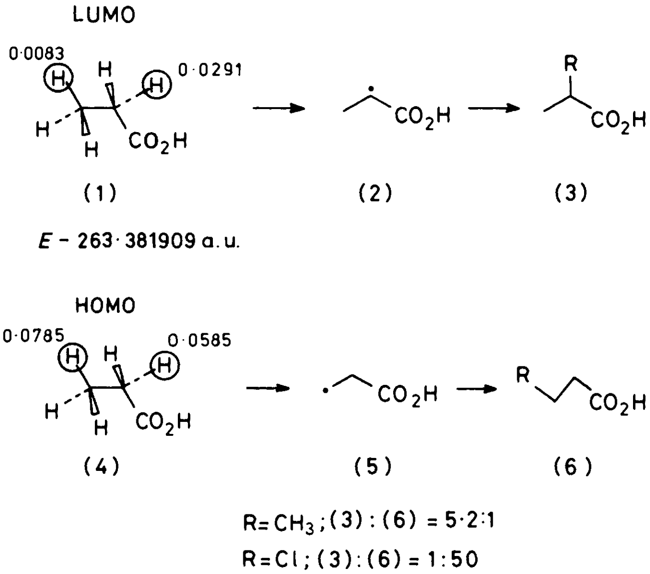

FIGURE 1 Hydrogen atomic sphere charges (electrons, radius 0.5 Å) for the HOMO and LUMO in propionic acid, and preferred hydrogen abstractions. Unspecified charges which are not equal by symmetry are near zero

Using these results the observation [8] that methyl radicals abstract hydrogen mainly from C-2 while chlorine atoms do so mainly from C-3 can be explained. For chlorine the important interaction is with the HOMO and the greatest charge in this orbital occurs for a hydrogen attached to C-3; methyl, because of the lower electronegativity of carbon, is much less electrophilic, and interaction with the LUMO is becoming important. For this orbital, abstraction from C-2 is strongly favoured and this serves to counterbalance the slight preference for C-3 abstraction in the HOMO.

A quantitative measure of the electrophilicity of a radical is provided in simple MO theory by the energy of the SOMO. However, the orbital approximation is a bad

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† Part 2, ref. 2.

one for radicals (as evidenced by the presence of appreciable unpaired spin density at C-2 in the allyl radical, observed by e.s.r.) due to the non-applicability of Brillouin's theorem. For open shells the ground state can interact with singly excited states. In *ab initio* calculations the restricted Hartree–Fock method is therefore abandoned and separate wavefunctions are obtained for electrons of α- and of β-spin (unrestricted Hartree–Fock). Each of these is separately factorised into one-electron functions, so pairing of electrons does not occur. Charge densities are calculated from each wavefunction, added to give the total charge density, and the difference is taken to give the unpaired spin density. This latter quantity is found to agree quite well with the e.s.r. data.

An attempt to correlate the calculated (GAUSSIAN 76; STO-3G) energy of the highest one-electron function (by convention always of α-spin) with electrophilicity of a series of radicals is shown in the Table. (It should be remembered that not all of the unpaired spin is associated with this function, which would be the case if the orbital approximation were sound.) The radicals are arranged in order of increasing electrophilicity (reflected in a decreasing ρ value for hydrogen abstraction from *para*-substituted toluenes[9]). The correlation with α-HOMO energy is no worse than with ionisation potentials[4] (the latter are used in simple FO theory to estimate the energy of the 'SOMO'), but in both cases it is poor, illustrating the danger of discussing effects in terms of the 'SOMO' energy of a radical species. However, the much greater electrophilicity of the chlorine atom than of the methyl radical is clearly demonstrated, supporting the assumption we made earlier when considering hydrogen abstraction on propionic acid.

Radical α-HOMO energies, ionisation potentials, and ρ values for hydrogen abstraction from *p*-substituted toluenes

Radical	ρ	I.P. (eV)	α-HOMO energy (a.u.)
$Bu^t\cdot$	1.0	−6.9	−0.2644
$Et_3Si\cdot$	0.3	−7	−0.1446
$Ph\cdot$	−0.1	−9.2	−0.2794
$Me\cdot$	−0.1	−9.8	−0.3554
$H\cdot$	−0.1	−13.6	−0.4666
$Bu^tO\cdot$	−0.4	−12	−0.3581
$Bu^tOO\cdot$	−0.6	−11.5	−0.3531
$HO_2CCH_2\cdot$	−0.7	−10.9	−0.3628
$Cl\cdot$	−0.7	−13	−0.4463
$Cl_3C\cdot$	−1.5	−8.8	−0.3255

When ambident radicals are considered, the frontier orbital approach is no longer valid because of the orbital approximation breakdown. However, an analogous method which uses the unpaired (α — β) spin density can be employed. This would be equivalent to the frontier orbital method if the orbital approximation held, the values obtained being the density in the SOMO. Use of the Dean and Richards technique (in which sphere-charges are calculated from both α- and β-density matrices and the difference is taken) offers the usual advantages[1] over conventional partial charge methods which assign all the charge to individual atomic centres.

Figures 2 and 3 illustrate how this procedure works in practice. The examples are radical substitution in anisole, where the C-2 radical from acetic acid substitutes exclusively on carbon,[9] and coupling of *N*-methylpyridyl radicals, which takes place at C-4.[10] In both cases the site of reaction clearly corresponds to the greatest sphere charge (all spheres are centred on the respective nuclei and have a radius of 0.7 Å). UHF wavefunctions obtained from GAUSSIAN/76 with an STO-3G basis set are used. RHF energies (GAUSSIAN 80) are also given; in each case the result is significantly poorer.

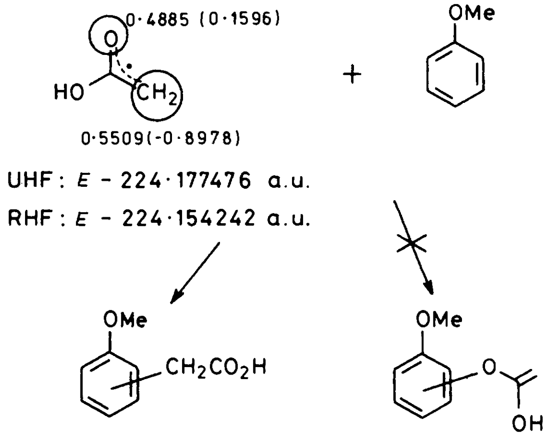

FIGURE 2 Ambident radical behaviour in aromatic substitution. Atomic sphere charges in electrons, radius 0.7 Å. SOMO coefficients in parentheses

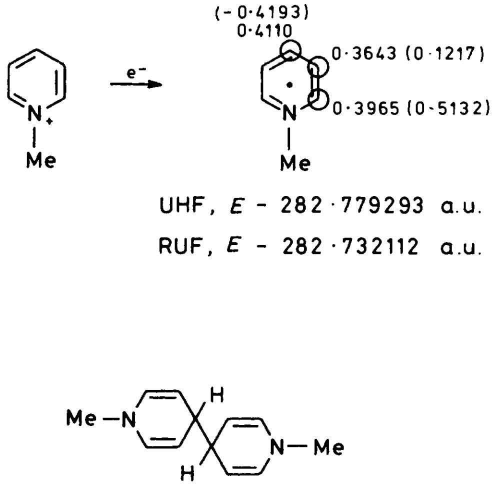

FIGURE 3 Ambident radical coupling. Atomic sphere charges in electrons, radius 0.7 Å. SOMO coefficients in parentheses

However, the RHF wavefunctions are more suitable for some applications since they are pure doublets and do not suffer from spin contamination.

Standard geometries[7] were used since the size of these molecules prohibits optimisation at the *ab initio* level. However, from experience we believe that the differences are sufficiently great to be still significant. Sphere charges do change on going from standard to fully optimised geometries, but usually only in the third and fourth decimal places, even for radicals and ionic species. Qualitative distinctions between the positions in a molecular are rarely altered.

In order to compare these results with the simple Frontier Orbital method at the same *ab initio* level the ' SOMO ' coefficients are also given for the atoms of interest. The squares of these numbers give a prediction of the unpaired spin density. While the method works well for the acetic acid radical it is unreliable in general as shown by the incorrect prediction in the case of *N*-methylpyridyl.

The sphere charge frontier orbital method is currently being applied to heterocyclic, pericyclic, and photochemical reactions.

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REFERENCES

[1] R. J. Elliott, V. Sackwild, and W. G. Richards, *J. Mol. Struct.*, 1982, **86**, 301.

[2] R. J. Elliott and W. G. Richards, *J. Mol. Struct.*, 1982, **87**, 211.

[3] S. M. Dean and W. G. Richards, *Nature*, 1975, **258**, 133; W. G. Richards and J. Wallis, *Proc. R. Soc. London, Sect. B*, 1977, **199**, 291; J. Wallis, QCPE, 1981, **13**, 411.

[4] I. Fleming, ' Frontier Orbitals and Organic Chemical Reactions,' Wiley, New York, 1976.

[5] J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. G. Newton, QCPE, 1978, **11**, 368.

[6] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[7] L. E. Sutton, ' Tables of Interatomic Distances and Configurations in Molecules and Ions,' Chem. Soc. Spec. Publ., 1956, No. 11; 1959, Supplement No. 18.

[8] H. Magritte and A. Brylants, *Ind. chim. belge*, 1957, **22**, 547.

[9] E. I. Heiba, R. M. Dessau, and W. J. Koehl, *J. Am. Chem. Soc.*, 1969, **91**, 138.

[10] B. Emmert, *Ber.*, 1909, **42**, 1997.