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A Quantitative Assessment of the Merostabilization Energy of Carbon-Centered Radicals

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Abstract: C-centered radicals RC(Don)(Acc) carrying both an electron-donor and an electron-acceptor substituent are significantly more stable than the corresponding symmetrical radicals $R\dot{C}(Don)_2$ and $R\dot{C}(Acc)_2$ in media of high dielectric constant, but not in the gas phase.

In 1964,[1] one of us suggested that, whereas carbanions are stabilized by electron-acceptor substituents and carbenium ions by electron-donor substituents, radical centers are specially stabilized by simultaneous substitution by both electron-donor *and* electron-acceptor substituents. This concept was denoted "merostabilization", developed by qualitative valence bond, molecular orbital, and Linnett double quartet theories and supported by the prediction and synthesis of new merostabilized radicals.[2] An analogous concept for nitrogen-centered "push–pull" radicals was independently developed by Balaban,[3] who used it to predict new nitrogen radicals. The theoretical idea behind these concepts had been formulated by Dewar[4] in 1952 but had remained neglected. More recently, merostabilized radicals have been the subject of much attention,[5] significantly assisted by extensive experimental work by Viehe.[6,7]

However, there has been much controversy regarding the amount, and indeed the reality, of the stabilization energy of merostabilized radicals.[8] The latest *published* theoretical calculations[9] disclose no appreciable extra stability. Although Leroy now believes[10] that such radicals generally have a somewhat larger stabilization energy than the sum of the stabilization energies of the corresponding monosubstituted species, and Clark[11] also finds small extra stabilizations, considerable skepticism was expressed at the recent NATO Conference ("Substituent Effects on Radical Stabilization") in January 1986 regarding the existence of an appreciable energetic stabilization.

In our initial publications,[2] the importance of charge-separated forms which allowed delocalization of the radical center over *all* the atoms in a conjugated chain (rather than at each alternate atom) was specifically emphasized and the comparison made to the charge delocalization in merocyanine dyes (whence the name). In view of the present activity and interest in merostabilized radicals,[5] we have now carried out calculations on a variety of them, taking into account solvation effects which are expected to greatly influence the importance of charge-separated canonical forms.[12]

We suggest that the merostabilization energy of a radical $\dot{C}RXY$ should be defined by eq 1, which refers this energy to that of the corresponding symmetrically substituted radicals.

$$\Delta E_M = E_{CRXY} - 0.5(E_{CRX_2} + E_{CRY_2}) \quad (1)$$

We have taken into account nonspecific or macroscopic solvation via the self-consistent reaction-field (SCRF) formulization.[13] The Hamiltonian H_{rf} of the molecule in the dielectric medium has the following form

$$H_{rf} = H_0 + H_1 \quad (2)$$

Table I. The INDO UHF SCRF Calculated Properties of Some Dihomosubstituted Radicals

radical	dielectric constant of solvent	total energy (hartree)	rel energy (kcal/mol)	dipole moment (D)
1. $CH(CN)_2$	1	−40.704 69	(0)	2.842
	80	−40.726 48	−13.7	3.511
2. $CH(OH)_2$	1	−41.729 64	(0)	0.889
	80	−41.732 99	−2.1	1.006
3. $CH(OCH_3)_2$	1	−57.834 85	(0)	3.392
	80	−57.858 73	−15.0	3.853
4. $CH(NH_2)_2$	1	−30.847 59	(0)	2.840
	80	−30.870 65	−14.4	3.314

where H_0 is the Hamiltonian of the isolated molecule and the perturbation term H_1 describes its interaction with the solvent polarization electric field (reaction field) around this molecule in solution. For a long-living species with the relaxation or half-life time $\tau \gg 10^{-11}$ s

$$H_1 = g(\epsilon)\langle\phi|\mu|\phi\rangle\mu \quad (3)$$

where ϕ denotes the electronic wave function of the solute molecule at the previous step of SCRF procedure, and μ is the dipole

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[1] The early development of these ideas is contained in the MSc Theses of R. W. Baldock (University of East Anglia, 1965) and of P. Hudson (University of East Anglia, 1971) (see also Ph.D. Thesis of P. Hudson, University of East Anglia, 1973).

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[4] Dewar, M.J.S., *J. Am. Chem. Soc.*, **1952**, 74, 3353.

[5] See, e.g.: *Substituent Effects on Radical Stabilization*, Proceedings of the NATO Conference held in January, 1986, at Louvain-la-Neuve, in press.

[6] Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917. Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.

[7] Viehe has suggested[6] that merostabilized radicals be referred to as "captodative".

[8] See, e.g.: Crans, D.; Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* **1980**, *21*, 3681. Klessinger, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 908.

[9] Leroy, G.; Peeters, D. *J. Mol. Struct.* **1981**, *85*, 133. Leroy, G.; Peeters, D.; Vilante, C. *J. Mol. Struct.* **1982**, *88*, 217. Leroy, G. *Int. J. Quant. Chem.* **1983**, *23*, 271.

[10] The use of second-order perturbation theory suggests small amounts of additional stabilization in the gas phase; Leroy, G., paper presented at NATO workshop on Radical Stabilization Effects, Louvain-la-neuve, Jan. 1986, and in press in the proceedings of this conference.

[11] Clark, T., see ref 10.

[12] As pointed out very recently by the following: Olson, J. B.; Koch, T. H. *J. Am. Chem. Soc.* **1986**, *108*, 756.

[13] Tapia, O.; Goscinski, O. *Mol. Phys.* **1975**, *29*, 1653. Tapia, O. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1982; Vol. 3, Chapter 2. Karelson, M. M. *Organic Reactivity (Tartu)* **1980**, *17*, 357.

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Table II. The INDO UHF SCRF Calculated Properties of Some Captodative Radicals

radical	dielectric constant of solvent	total energy (hartree)	rel energy (kcal/mol)	dipole moment (D)	$\Delta E_M(1)$ (kcal/mol)
1. CH(CN)OH	1	−41.21226	(0)	3.279	3.1[a]
	80	−41.26855	−35.5	5.168	−24.4
2. $CH(CN)OCH_3$	1	−48.91932	(0)	4.341	1.2
	80	−48.99797	−49.4	6.796	−28.8
3. $CH(CN)NH_2$	1	−35.76695	(0)	3.150	5.7
	80	−35.81012	−27.1	5.039	−7.3

[a] This number is in a good accordance with the earlier value (ΔE_M = 3.31 kcal/mol),[8] obtained from the ab initio UHF full geometry optimization calculations with the 4-31G basis set.

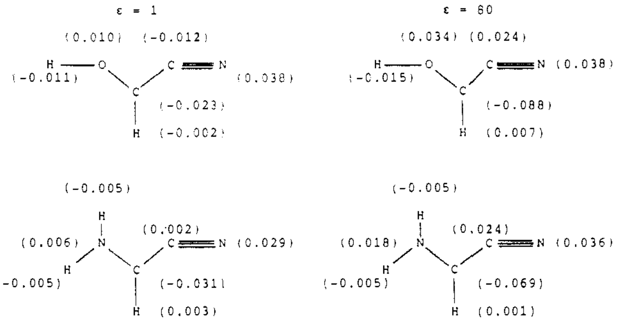

Figure 1. The INDO UHF SCRF calculated spin density differences of the merostabilized radicals in different dielectric media.

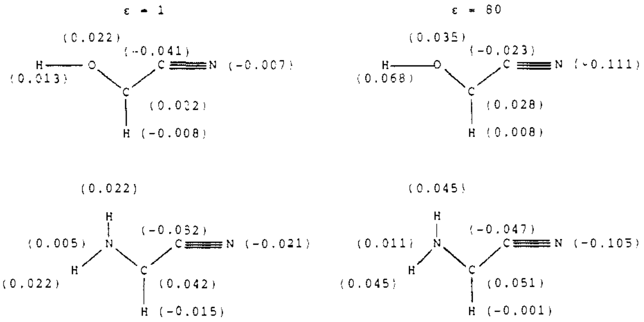

Figure 2. The INDO UHF SCRF calculated charge density differences of the merostabilized radicals in different dielectric media.

moment operator. The dielectric permittivity tensor $g(\epsilon)$ is a parameter of the macroscopic dielectric constant of the solvent, ϵ

$$g(\epsilon) = \frac{\epsilon - 1}{(2\epsilon + 1)a_0^3} \qquad (4)$$

In the last formula (eq 4), a_0 denotes the radius of the (presumed spherical) cavity in the solvent, into which the solute molecule is embedded.

In each calculation the corresponding cavity radius was estimated from the intrinsic volume V_0, itself calculated from the refractivity of the molecule investigated[14]

$$a_0 = (3V_0/4\pi)^{1/3} \qquad (5)$$

The set of modified Hartree–Fock equations

$$H_{rf}\psi_i = \epsilon_i\psi_i \qquad (6)$$

was then solved by the usual self-consistent-field procedure to obtain the MOs $\{\psi_i\}$ and corresponding orbital energies $\{\epsilon_i\}$. The SCRF approach was used by us in the framework of INDO and INDO CI[15] methods with full geometry optimization. A more complete discussion of these techniques will be given elsewhere.[16]

The results of these SCRF UHF INDO calculations on some organic radicals are given in Tables I and II. The spin and charge distribution differences of these radicals in different dielectric media are illustrated by the data in Figures 1 and 2.

There is significant stabilization of all of the radicals in the high dielectric constant medium (ϵ = 80). However, the value of this stabilization energy is much larger in the case of merostabilized radicals (cf. Tables I and II). This leads now to important differences in the merostabilization energies calculated according to eq 1.

In agreement with the literature data mentioned above,[9] we observe no additional stabilization of captodative radicals in the gas phase at the Hartee–Fock molecular orbital level.[10] In fact our calculations indicate a small destabilization of these radicals compared to the corresponding symmetrical radicals. However, in a high dielectric constant continuum, substantial stabilization (7–28 kcal/mol) is predicted (cf. Table II). The physical reason for this stabilization is the higher polarization (and dipole moment) of the donor–acceptor substituted radicals in a high dielectric constant medium in comparison with the corresponding dihomosubstituted radicals. The dipole moment of symmetrically substituted radicals increases only by 15–20% as the dielectric constant increases from ϵ = 1 to 80. The corresponding change for merostabilized radicals is 50–60%. This remarkable difference in the charge distribution is reflected by the greater charge delocalization (see Figure 1) and also by the greater unpaired electron delocalization (see Figure 2) in the merostabilized radicals in solution.

It follows that the merostabilization of radicals in solution is essentially caused by the environmental effects on their electronic structure and stability. This provides another highly experimentally significant example of the importance of solvation in explaining and predicting the intrinsic electronic properties in solution. It must be emphasized finally that appreciable merostabilization of radicals is not predicted through calculations that do not include the solvent.[9-11]

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