Ground States of Conjugated Molecules. IX.[1] Hydrocarbon Radicals and Radical Ions[2]

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Abstract: The SCF–MO method described in previous papers[4] of this series has been extended to open-shell systems, in particular hydrocarbon radicals and radical ions. The calculations were carried out by a modified closed-shell procedure in which the unpaired electron is replaced by two half-electrons of opposite spin. The results are in good agreement with experimental data for the heats of formation of radicals and electron affinities and ionization potentials of even-alternant hydrocarbons; they also suggest that the differences between spectroscopic and electron-impact values for ionization constants are due to the former being adiabatic values, and the latter vertical ones. A theoretical justification for the half-electron model is given, and it is also used to explain the success of the PMO method.[5]

Attempts to discuss the heats of formation of conjugated radicals in terms of MO theory have until now been limited to crude HMO calculations. The purpose of this paper is to present a SCF–MO treatment which seems to give very satisfactory results for a wide range of hydrocarbon radicals and radical ions. The basis of this approach is a version of the Pople SCF MO method which has been described in earlier papers[4] of this series, and which has been shown to account with remarkable accuracy for the ground-state properties of a wide range of conjugated molecules[1,4,6] of closed-shell type. Here we describe a simple modification of the method which allows it to be applied with similar success to open-shell systems.

The radicals treated here are hydrocarbon radicals, such as allyl or benzyl, and ion radicals derived from neutral hydrocarbons by loss, or gain, of an electron. The heats of formation of various radicals have been measured in recent years; those of the ions can be inferred from the heats of formation of the parent hydrocarbons, together with the experimentally determined ionization potentials or electron affinities. Most previous attempts to calculate ionization potentials or electron affinities have been based on the use of Koopmans' theorem.[7] For reasons that will become apparent presently, this procedure is not applicable here. However, our method provides direct estimates of the heats of formation of the ion radicals, which, together with similar estimates for the parent hydrocarbons, allow the ionization potentials and electron affinities to be calculated. Since our procedure now gives heats of formation of neutral hydrocarbons with an accuracy of *ca.* ±0.005 ev per carbon atom, comparisons of the calculated and observed ionization potentials and electron affinities should provide a further stringent test of the calculations for open-shell systems.

Theoretical Method

Previous papers[1,4,6] of this series have described a semiempirical SCF–MO treatment of the π electrons in conjugated molecules, using the Hückel σ,π approximation; our objective here is to extend this treatment to radicals and radical ions, in particular to their heats of formation.

Previous studies of radicals by the SCF–MO method[8] have been based almost exclusively on the use of the open-shell SCF–MO treatment proposed by Brickstock and Pople,[9] in which electrons of different spin occupy different sets of MO's. This approach has the advantage of accounting for the appearance of negative spin densities, *e.g.*, at the central atom of the allyl radical; it also provides a formally correct solution to the problem of representing open-shell systems by single Slater determinants. The main theoretical objection to it lies in the fact that such single determinants are not in general eigenfunctions of the operator S^2; to obtain a satisfactory wave function for an open-shell system, it is therefore necessary either to project out from the single Slater determinant the contribution due to the lowest multiplet, or to annihilate contributions of higher multiplets. As yet only the latter approach has been tried in the case of large organic radicals, and usually only the lowest contaminating multiplet has been annihilated.[8]

In our initial studies we applied the open-shell SCF–MO method to radicals, with and without annihilation of contributions by the higher spin states, and using the parameters that had been found appropriate for closed-shell molecules.[1,4,6] The results were, however, unsatisfactory, the calculated heats of atomization for allyl and benzyl being too great by 0.5 ev. Further consideration suggested the following explanation for this disappointing result.

The Hartree–Fock method does not allow for electron correlation, other than by its use of antisymmetrized

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(1) Part VIII: M. J. S. Dewar, G. J. Gleicher, and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **88**, 1349 (1966).

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(3) National Institutes of Health Postdoctoral Fellow, 1966–1967.

(4) (a) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); (b) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685 (1965).

(5) M. J. S. Dewar, *ibid.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

(6) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 692, 3255 (1965); *Tetrahedron*, **21**, 1817, 3423 (1965); *Tetrahedron Letters*, **50**, 4503 (1965); *J. Chem. Phys.*, **44**, 759 (1966); M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965).

(7) See, *e.g.*, (a) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953); (b) B. Roos and P. N. Skancke, *Acta Chem. Scand.*, **21**, 233 (1967); (c) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

(8) (a) T. Amos and L. C. Snyder, *ibid.*, **41**, 1773 (1964); (b) L. C. Snyder and T. Amos, *ibid.*, **42**, 3670 (1965).

(9) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 268 (1954).

wave functions; consequently, *a priori* calculations of this kind give very poor results for the energies and heats of atomization of molecules. The fact that our method[1,4,6] gives heats of atomization with high precision ($<0.1\%$) therefore shows that it must in some way allow for the additional effects of correlation. This allowance is clearly due to the presence of parameters, suitable adjustment of which apparently provides the required compensation over the whole range of closed-shell conjugated systems. The open-shell SCF–MO method differs from the closed shell one in that it does provide additional allowance for correlation through its use of different orbitals for electrons of different spins. If then we carry out a calculation by the open-shell SCF–MO method, using the closed-shell parameters, we will in effect be allowing for these additional effects of correlation twice over, so the calculated heats of atomization are correspondingly too large.

This argument suggests that open-shell systems could be treated satisfactorily in one of two ways. Either we could use the open-shell SCF–MO method with a set of parameters appropriate to it, or we could use the closed-shell parameters together with some treatment which does not introduce additional allowance for correlation. The second approach is clearly the more attractive since it involves no new parameters.

In the closed-shell SCF–MO treatment, each MO is either empty, or symmetrically occupied by two electrons of opposite spin. Open-shell systems cannot be treated directly in this way because the symmetry of the orbital occupation is broken; one orbital is unsymmetrically occupied by an electron which has either α spin or β spin. If we are to treat radicals by the closed-shell method, we must therefore get rid of this asymmetry. In order to do this we must represent the molecule by a wave function in which the spin of the unpaired electron is uncertain, and one obvious solution would be to use the function ψ given by

$$\psi = \frac{1}{\sqrt{2}}(\psi^{\alpha} + \psi^{\beta}) \qquad (1)$$

when ψ^{α} and ψ^{β} are "closed-shell" Slater determinants, constructed from the same set of MO's, in which the unpaired electron has respectively α or β spin. This kind of approach to open-shell problems has been discussed in detail by Roothaan,[10] who has derived equations for the general case where there are m doubly occupied orbitals and n singly occupied ones. The objection to this approach is that it involves a kind of eigenvalue problem different from those in the usual closed- and open-shell SCF treatments, and it would therefore require a special program for its solution. Consequently, the following approximate solution seems to have much to recommend it, since the results must be almost identical with those that would be obtained by the Roothaan method and since the calculations can be carried out by the usual closed-shell method, with one very small modification.

Consider the closed-shell treatment of a radical with one unpaired electron. Denote by ψ_{μ} the doubly occupied MO's, and by ψ_{o} the singly occupied one. If we use the Roothaan function of eq 1, the total energy (E_1) is given by

$$E_1 = 2\sum_{\mu} E_{\mu}^{\mathrm{c}} + E_{\mathrm{o}}^{\mathrm{c}} + \sum_{\mu}\sum_{\nu}(2J_{\mu\nu} - K_{\mu\nu}) + \sum_{\mu}(2J_{\mu\mathrm{o}} - K_{\mu\mathrm{o}}) \qquad (2)$$

where E_{μ}^{c} is the core energy of an electron occupying the MO ψ_{μ}, and $J_{\mu\nu}$ and $K_{\mu\nu}$ are the usual Coulomb and exchange integrals. Now the energy (E_2) of a closed-shell system constructed from the MO's ψ_{μ} is given by

$$E_2 = 2\sum_{\mu} E_{\mu}^{\mathrm{c}} + \sum_{\mu}\sum_{\nu}(2J_{\mu\nu} - K_{\mu\nu}) \qquad (3)$$

In our program, the occupancy of the orbitals is specified by supplying as data the number (n_{μ}) of electrons occupying the orbital ψ_{μ}; in a closed-shell system, $n_{\mu} = 2$ for all occupied MO's and zero for empty ones. In this case the total energy E_2 is given by the expression

$$E_2 = \sum_{\mu} n_{\mu}E_{\mu}^{\mathrm{c}} + {}^{1}/_{4}\sum_{\mu}\sum_{\nu} n_{\mu}n_{\nu}(2J_{\mu\nu} - K_{\mu\nu}) \qquad (4)$$

(This of course is equivalent to eq 3.)

Suppose we try to treat our radical with this program, simply setting n_{o} (the occupation number of ψ_{o}) equal to unity instead of two. The total energy (E_3) is then given by eq 5. Apart from the small final term ${}^{1}/_{4}J_{\mathrm{oo}}$,

$$E_3 = \sum_{\mu} 2E_{\mu}^{\mathrm{c}} + E_{\mathrm{o}} + {}^{1}/_{4}\sum_{\mu}\sum_{\nu} 4(2J_{\mu\nu} - K_{\mu\nu}) + {}^{1}/_{4}\sum_{\mu} 2(2J_{\mu\mathrm{o}} - K_{\mu\mathrm{o}}) + {}^{1}/_{4}\sum_{\nu} 2(2J_{\nu\mathrm{o}} - K_{\nu\mathrm{o}}) + {}^{1}/_{4}(2J_{\mathrm{oo}} - K_{\mathrm{oo}}) = 2\sum_{\mu} E_{\mu}^{\mathrm{c}} + E_{\mathrm{o}} + \sum_{\mu}\sum_{\nu}(2J_{\mu\nu} - K_{\mu\nu}) + \sum(2J_{\mu\mathrm{o}} - K_{\mu\mathrm{o}}) + {}^{1}/_{4}J_{\mathrm{oo}} \qquad (5)$$

this is identical with the correct Roothaan expression of eq 2. Since our program solves the problem of minimizing the total energy with respect to variation of the MO's, subject to the condition that they remain orthogonal, the solution for the radical will differ from that given by the Roothaan procedure only insofar as the final term ${}^{1}/_{4}J_{\mathrm{oo}}$ is affected by changes in the orbitals. Since the absolute magnitude of this term is in any case small ($\sim$1 ev), the changes in it due to changes in the orbitals are likely to be negligible. If so, our closed-shell procedure will give results essentially identical with those that would be given by the more rigorous treatment, and this by using a standard closed-shell program. Of course, one small modification has to be made; the total energy computed by the program will be E_3, which differs from E_1 by the first-order term ${}^{1}/_{4}J_{\mathrm{oo}}$ as well as by the second-order terms that we are neglecting. Our estimate (E_1') of the total energy is therefore given by

$$E_1' = E_3 - {}^{1}/_{4}J_{\mathrm{oo}} \qquad (6)$$

It is a trivial matter to include this correction in the program.

While we have presented this approach in a formal manner, it was in fact arrived at from a consideration of the following physical model. Instead of using the two-configuration function of eq 1, one could represent the radical symmetrically by a single determinant if one replaced the unpaired electron in it by two "half-electrons" of opposite spin. A "half-electron" in this sense would be defined as an imaginary particle with half the charge and twice the mass of an electron, the orbital energy of such a particle, occupying the MO ψ, being

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

$E_\mu/2$. If one calculates the total energy of the radical for this model, one finds that it is in fact equal to E_3 (eq 5). This of course is what one would expect, for the closed-shell treatment corresponds to a situation where the α- and β-spin electrons occupy the same set of orbitals in pairs, the number of electrons of each type in a given MO ψ_μ being $n_\mu/2$. If then we set $n_o = 1$, this must imply that the orbital ψ_o is occupied by half an electron of α spin and half an electron of β spin. We can see on this basis how the final term in eq 5 arises, and why it has to be omitted if we are to get a valid estimate of the total energy of the actual radical; it represents the (spurious) repulsion between the two half-electrons occupying ψ_o.

Since it is useful to have some term to describe this approximation, to distinguish it from, *e.g.*, the Roothaan treatment, and since the physical model on which it is apparently based seems entertaining, we have, with some trepidation, termed it the "half-electron method." Here we have applied the procedure solely to radicals containing one unpaired electron; it can obviously be extended to systems with more than one unpaired electron, *e.g.*, triplet states.

The calculations were carried out using the closed-shell SCF–MO program described previously,[1,4,6] the only modification being an additional subroutine to calculate the correction term $(-{}^{1}/_{4}J_{oo})$ in the expression for the total energy. The parameters used were close to the PPP set in the earlier papers; they were taken from a forthcoming paper[11] describing revised calculations for closed-shell hydrocarbons. In the earlier treatment,[1,4,6] the carbon–carbon σ bond energy was in effect treated as an additional parameter, although logically one should use the value given by the thermocycle used to estimate β. The modified parameters[11] make the treatment self-consistent in this respect.

Although this treatment of open-shell systems should give good estimates of energies, it need not of course give even approximately correct values for the Hartree–Fock orbital energies (see eq 3–5). Ionization potentials and electron affinities cannot therefore safely be found by using Koopmans' theorem; they must be estimated by difference from the total energies of the parent hydrocarbon and the corresponding positive or negative ion.

Discussion and Results

One of the disappointing aspects of this investigation was the paucity of data available to test the validity of our calculations for neutral radicals. Allyl and benzyl are the only two π-hydrocarbon radicals for which the heats of formation are known. The ground-state energies of three other conjugated hydrocarbon radicals, cyclohexenyl, cyclohexadienyl, and α-phenethyl, have been reported, but these are systems which contain σ bonds other than the ones which make up the σ framework of the conjugated systems. Table I shows the bond energies which were added to the energies calculated by the varied bond-length method described in paper II of this series.[4b] They correspond to localized bonds outside the π system and its σ framework. The calculated and observed heats of formation for these five species are presented in Table II. The errors quoted in the observed values represent the estimates of the authors in each case. The calculated values are in quite good agreement with the observed heats of formation, falling within the experimental error in all cases.

Table I. Bond Energies for Localized Bonds

Type of bond	E, ev	Source
sp^{2}C–H($E_{\mathrm{CH}^{\mathrm{u}}}$)	4.4375	[ΔH_a(ethylene) − E_{DB}]/4
sp^{3}C–H($E_{\mathrm{CH}^{\mathrm{s}}}$)	4.2816	[2ΔH_a(ethane) − H_a(propane)]/4
sp^{3}C–sp^{2}C	3.8417	[ΔH_a(2-butene) − 2$E_{\mathrm{CH}^{\mathrm{u}}}$ − 6$E_{\mathrm{CH}^{\mathrm{s}}}$ − E_{DB}]/2
sp^{3}C–sp^{3}C	3.5647	[ΔH_a(propane) − 8$E_{\mathrm{CH}^{\mathrm{s}}}$]/2

Table II. Heats of Formation of Hydrocarbon Radicals

Radical	H_f, ev Calcd	 Obsd	Ref
Allyl	32.08	31.92 ± 0.16	*a*
Benzyl	65.64	65.78 ± 0.29	*b*
α-Phenethyl	77.89	78.19 ± 0.27	*c*
Cyclohexenyl	63.71	63.54 ± 0.22	*d*
Cyclohexadienyl	58.30	58.14 ± 0.22	*d*

[a] R. J. Akers and J. J. Throssell, *Trans. Faraday Soc.*, **63**, 124 (1967). [b] R. Walsh, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 650 (1966). [c] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [d] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

The second method of testing the utility of this half-electron method is to compare ionization potentials calculated by this method with the experimentally observed ones. In order to maintain the use of physically real constants in our semiempirical treatment, we have equated the ionization potential of methyl radical, 9.84 ev,[12] to $W(2p)$[4a] for a trivalent carbon atom. As stated earlier, one must recalculate the self-consistent orbitals and recompute the energy of the cation to obtain correct ionization potentials. There are two ways of doing this. First, one can calculate the energy of the ion, at the same time allowing the bond lengths to vary to a new minimum. This allows both for different orbitals and for different geometries in the neutral species and cations. Adiabatic ionization potentials should be calculated in this manner. Vertical ionization potentials, on the other hand, should allow for changes in orbitals but *not* changes in geometry. This was accomplished by calculating the energy of the neutral species by the varied bond-length procedure described in part II of this series,[4b] and then recalculating the cation as a fixed geometry problem using these bond lengths.

The spectroscopic method of determining ionization potentials as the convergence limit of a molecular Rydberg series is an adiabatic method. Since the values obtained spectroscopically are in very close agreement with the values obtained by photoionization and photoelectron spectroscopy, these also yield adiabatic ionization potentials. Electron-impact data on the other hand always given slightly higher values of ionization potentials, and this has often been explained on the basis that these are vertical ionizations. Table III shows the calculated and observed vertical and adiabatic ionization potentials, the total bonding energies of the ground states, and the electron affinities of a number of molecules and radicals.

Only electron-impact data are available for the free radicals; fortunately this presents no problem. Since

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(11) M. J. S. Dewar and C. R. deLlano, work in course of publication.

(12) G. Herzberg, *Proc. Roy. Soc.* (London), A262, 291 (1961).

Table III. Calculated and Observed Ionization Potentials

Compound	Ground-state energy	Adiabatic IP[a] Calcd	Adiabatic IP[a] Obsd	Ref	Vertical IP Calcd	Vertical IP Obsd[b]	Ref	A
Benzene	−30.532	9.22	9.24 (PI)	*t*	9.35	9.38	*s*	−0.74
			9.24 (PS)	*c*				
Naphthalene	−55.111	8.30	8.12 (PI)	*t*	8.45	8.26	*s*	0.07
Anthracene	−79.524	7.72	7.38 (PI)	*p*	7.83	7.55	*s*	0.65
			7.15 (S)	*d*				
Phenanthrene	−79.850	8.10			8.28	8.03	*s*	0.27
Tetracene	−103.865	7.31	6.88 (PI)	*p*	7.42			1.06
Styrene	−40.410	8.56	8.47 (PI)	*u*	8.71	8.86	*k*	0.19
			8.42 (PS)	*q*				
Biphenyl	−65.378	8.31	8.27 (PI)	*u*	8.45	8.30	*n*	0.06
Azulene	−53.973	7.54	7.43 (S)	*e*	7.63	7.72	*r*	1.03
			7.41 (PI)	*i*				
Ethylene	−5.560	9.90	10.48 (PS)	*c*	10.14	10.56	*g*	−1.53
			10.52 (PI)	*t*				
cis-Butadiene	−15.461	8.97	8.75 (S)	*o*	9.14			−0.57
trans-Butadiene	−15.427	8.83	9.08 (PS)	*c*	9.02	9.18	*f*	−0.46
			9.07 (PI)	*t*				
Hexatriene	−25.311	8.24	8.26 (S)	*l*	8.43			0.13
Octatetraene	−35.197	7.89	7.80 (S)	*l*	8.08			0.48
Allyl	−9.893	8.32			8.32	8.16	*j*	0.05
Pentadienyl	−19.912	7.89			7.89	7.73	*m*	0.48
Benzyl	−34.576	7.47			7.48	7.73	*j*	0.90
Benzhydryl	−69.588	6.91			6.91	7.32	*h*	1.40
α-Naphthylmethyl	−59.175	7.02			7.03	7.35	*h*	1.35
β-Naphthylmethyl	−59.115	7.12			7.14	7.56	*h*	1.25

[a] PI, photoionization; PS, photoelectron spectroscopy; S, spectroscopic. [b] All values are electron-impact data. [c] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964). [d] J. G. Angus and G. C. Morris, *J. Mol. Spectry.*, **21**, 310 (1966). [e] L. B. Clarke, *J. Chem. Phys.*, **43**, 2566 (1965). [f] J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **79**, 5848 (1957). [g] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, p 253. [h] A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 1052 (1960). [i] T. Kitigawa, H. Inokuchi, and K. Kodera, *J. Mol. Spectry.*, **21**, 267 (1966). [j] F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954). [k] J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952). [l] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (London), **A185**, 182 (1945). [m] A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959). [n] T. M. Sugden, A. D. Walsh, and W. C. Price, *Nature*, **148**, 373 (1941). [o] T. M. Sugden and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 76 (1945). [p] A. Terenin and F. Vilessov, *Advan. Photochem.*, **2**, 385 (1964). [q] D. W. Turner, *Advan. Phys. Org. Chem.*, **4**, 31 (1966). [r] R. J. Van Brunt and M. E. Wacks, *J. Chem. Phys.*, **41**, 3195 (1964). [s] M. E. Wacks and V. H. Dibeler, *ibid.*, **31**, 1557 (1959). [t] K. Watanabe, *ibid.*, **26**, 542 (1957). [u] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

the ionization of such a radical involves loss of a nonbonding electron, the geometries of the radical and ion should be very similar and so likewise should be the vertical and adiabatic ionization potentials. The errors in the calculated ionization potentials are about the same as those in the calculated heats of formation. The only serious deviation occurs in the case of ethylene; this may well be due to σ,π interactions which our treatment neglects, and which should be more important in small ions. Note that the calculated vertical and adiabatic ionization potentials differ by an almost constant amount, *ca.* 0.15 ev. This difference is about the same as that between ionization potentials measured spectroscopically, and by electron impact, a result in agreement with the explanation adopted here.

Table IV. Calculated and Observed Electron Affinities

Compound	Ground-state energy	Electron affinity, ev Obsd[a]	Electron affinity, ev Calcd[b]	Ionization potentials Adiabatic	Ionization potentials Vertical
Naphthalene	−55.111	0.15	0.07	8.30	8.45
Anthracene	−79.524	0.55	0.65	7.72	7.83
Phenanthrene	−79.850	0.31	0.27	8.10	8.28
Benz[*a*]anthracene	−104.333	0.70	0.64	7.73	7.85
Benzo[*c*]phenanthrene	−104.531	0.54	0.38	7.99	8.09
Chrysene	−104.532	0.42	0.51	7.86	8.00
Tetracene	−103.865	1.15	1.06	7.31	7.42
Triphenylene	−104.691	0.28	0.26	8.12	8.24
Pyrene	−94.253	0.58	0.66	7.71	7.82
Benzo[*a*]pyrene	−118.861	0.83	0.93	7.49	7.56
Benzo[*c*]pyrene	−119.130	0.49	0.61	7.76	7.86
Dibenz[*a*,*h*]-anthracene	−129.112	0.68	0.65	7.72	7.84
Dibenz[*a*,*j*]-anthracene	−129.112	0.69	0.58	7.79	7.88

[a] Data of ref 7c. [b] $A = 9.66 - (E_b^{\text{anion}} - E_b^{\text{parent}})$; see text.

A third way of testing our procedure is provided by comparisons of calculated and observed electron affinities. Becker and Chen[7c] have recently published a number of electron affinities for alternant hydrocarbons. These were determined in solution so that an unknown solvation energy difference between the two species must be absorbed into an empirically determined constant, the electron affinities (A) being given by

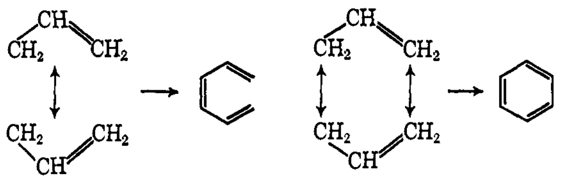
$$A = K - (E_b^{\text{anion}} - E_b^{\text{parent}})$$

Here the difference in solvation energy is assumed to be the same for all the compounds and their ions, K therefore having a constant value (9.66 ev). Table IV presents the calculated and observed electron affinities. The standard deviation of the calculated values is 0.09 ev. This represents the sum of the probable errors in calculating the heats of formation of an anion and the corresponding neutral species. Since the error for the alternant hydrocarbons is about 0.005 ev per carbon atom, heats of formation of anion radicals can apparently be estimated with comparable accuracy. The maximum error (0.16 ev) appears in the case of benzo[*c*]phenanthrene. This is probable due either to a difference in steric strain between the hydrocarbon and the anion or to an abnormal solvation energy difference as a result of the peculiar shape of this molecule. Table IV also lists calculated ionization potentials.

Justification for the PMO Method

Fifteen years ago, one of us[5] developed a general semiquantitative treatment of organic chemistry based on the application of perturbation theory to the Hückel MO (HMO) method. This perturbational MO (PMO) treatment has proved remarkably successful in practice; indeed, it often works better than the HMO method itself. A good example is provided by the phenomenon of aromaticity. The HMO method fails completely in this connection, regularly predicting large resonance energies for molecules (*e.g.*, pentalene and heptalene) which are not aromatic. The PMO method invariably predicts correctly[13] whether given molecules should be aromatic, nonaromatic, or antiaromatic. Indeed, until the development of our SCF–MO procedures,[1,4,6] the PMO method was the only one which could be used satisfactorily in this connection, and recently it has been shown[13] that a similar procedure can be used to account in a rather simple way for the course of electrocyclic reactions. This success raises a rather puzzling point; how can the PMO method be superior to the HMO method, given that the former is but a first approximation to the latter? The success of our half-electron treatment of open-shell systems seems to provide an answer to this conundrum.

The PMO treatment compares the energies of related even conjugated hydrocarbons by constructing them by union of common odd fragments. For example, the π energies of benzene and hexatriene can be compared by estimating the changes in π energy when two allyl radicals unite to form one or other of the two even species; *viz.* eq 7. To a first approximation, the change in π energy during union of two such odd-alternant radicals arises from mutual interaction of their NBMO's, which, in the HMO approximation, are degenerate. The interaction energy can be calculated in a very simple manner by first-order perturbation theory, since the coefficients of AO's in the NBMO of an odd-alternant hydrocarbon radical can be found at once by a procedure of Longuet-Higgins.[14] Now the special properties of NBMO's in the HMO method do not carry over into the open-shell SCF–MO treatment; in particular, the singly occupied MO's of different odd-alternant hydrocarbon radicals (allyl, benzyl, etc.) do not have identical energies. It therefore seems at first sight that the PMO treatment must indeed be based on the HMO approximation and so should not be superior to it.


(7)

However, the odd systems introduced in the PMO treatment do not need to be normal chemical species. All we need are suitable common building blocks that can be used to construct the pairs of even systems we are comparing. We are therefore at liberty to use "closed-shell" radicals for this purpose, in which the unpaired electrons are replaced by pairs of half-electrons. It is very easily shown that odd-alternant hydrocarbon radicals of this type obey the pairing theorem, and in particular that the half-electrons in them occupy MO's of identical energies, the coefficients in which are given by the usual Longuet-Higgins[14] procedure. The PMO treatment can therefore be regarded as a first approximation not to the HMO method, but to the Pople SCF–MO method that has been developed in earlier papers of this series. Since this procedure is known to give very satisfactory values for the heats of formation of conjugated hydrocarbons of all kinds, it is not surprising that the PMO method should lead to a correspondingly satisfactory picture.

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The Reactivity of C_2O

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Abstract: Carbon suboxide has been photolyzed in mixtures of ethylene and one other gas. The relative reactivities determined by this direct competition support the values found by another method and disagree completely with an independent set of reactivities. Photolyzing at 3000 and at 2500 Å produces two different intermediates which are thought to be $C_2O(\tilde{X}^3\Sigma)$ and $C_2O(\tilde{a}^1\Delta)$. The reactivity of these intermediates with the olefins is compared with that of other singlet and triplet species. It is concluded that $C_2O(\tilde{X}^3\Sigma)$ is electrophilic, similar to $O(^3P)$ and $S(^3P)$. In contrast, $C_2O(\tilde{a}^1\Delta)$ is quite indiscriminate. The differences in reactivity found for $C_2O(\tilde{X}^3\Sigma)$ are primarily the result of differences in activation energy, although some steric effects are present.

Carbon suboxide, C_3O_2, undergoes a simple photochemical reaction with olefins.[1] A single carbon atom is inserted into the carbon–carbon double bond, giving an allene and two molecules of CO. The reactive intermediate is thought to be the C_2O molecule.[2]

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