Radical Stabilization Energies of Disubstituted Methyl Radicals. A Detailed Theoretical Analysis of the Captodative Effect

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Abstract: Theoretical calculations have been carried out on a large number of disubstituted methyl radicals and methanes. Radical stabilization energies (RSE's) have been calculated as the change in total energies of the species in the isodesmic reaction shown in eq 2. The differences between the calculated RSE's for the disubstituted methyl radicals and the sum of the RSE's of the corresponding singly substituted methyl radicals (indicated as ΔRSE's) provide an indication for the presence of any extra stabilization or destabilization present in the disubstituted methyl radicals. The results of the calculations indicate that allyl-type systems comprised of three AO's in the delocalized radical π system containing a single electron (i.e., a diacceptor radical Y-CH-Y in which Y is an acceptor group possessing a single AO) suffer significant destabilization compared to the sum of the RSE's of the two singly substituted radicals. The allyl-type systems containing three electrons (i.e., donor-acceptor substituted radicals X-CH-Y in which X is the donor and Y the acceptor group) possess considerable extra (captodative) stabilization. Allyl-type systems containing five electrons (i.e., didonor substituted radicals X-CH-X) suffer considerable destabilization. Butadiene-type systems comprised of four AO's in the delocalized radical π system containing three (Y-CH-C=Y) and five (X-CH-C=Y) electrons are indicated to be neither highly stabilized nor destabilized relative to the sum of the stabilizations present in the singly substituted radicals. These systems possess either slight stabilization or slight destabilization, depending on the electronegativity of the attached functions, the destabilization increasing with increasing electronegativity of the donor group and the stabilization increasing with increasing electronegativity of the acceptor group. Pentadienyl-type systems comprised of five AO's in the delocalized radical π system containing five electrons (i.e., π didonor substituted radicals Y=C-CH-C=Y) are indicated to possess slight extra stabilization except for the highly electronegatively substituted cyanoformyl- and diformylmethyl radicals. It is concluded that the captodative effect concept is not universally valid and that many of the experimental results claimed to support the captodative effect concept involve ground-state electronic effects and not electronic effects in the transition states for the reactions studied. An analysis of the use of resonance theory as the basis of the captodative effect is discussed.

Considerable effort has been expended in the studies of how various substituents interact with a radical center[1] and to determine quantitatively the amount of stabilization of the radical center that is provided by the substituent.[2] As experimentally determined thermodynamic stabilization energies are extremely difficult to obtain, theoretical approaches have been extensively used. These theoretical approaches have included the calculation of radical stabilization energies (RSE's) of monosubstituted methyl radicals[3] and stabilization energies (SE's).[4] The author's interest in this area has been stimulated by the observed effects of substituents on the relative rates of (2 + 2) cycloaddition reactions of substituted allenes, which proceed via the formation of diradical intermediates.[5] A review of the literature revealed that very little quantitative information was available concerning the thermodynamic stabilization energies of substituted radicals. Most of the available data had been derived from kinetic studies, which relate only differences in the energies between the ground states of the reactants and the transition states for the radical-forming reactions. It was obvious that the degree of the development of the radical center in the transition states varied substantially from reaction to reaction, giving rise to quite different estimates of the stabilization or resonance energy of a given substituted radical.[3] It was also obvious that conformational factors greatly affected the values of the stabilization energies observed. In order to gain

information on the stabilization of a radical center by various substituents, a theoretical study was undertaken to calculate radical stabilization energies (RSE's) of mostly monosubstituted methyl radicals, in which the RSE is defined as the change in the total energy for the isodesmic reaction shown in eq 1.[3] Reasonable

$$X_n\text{-}\dot{C}H_{3-n} + CH_4 \rightarrow X_n\text{-}CH_{4-n} + \dot{C}H_3 \qquad (1)$$
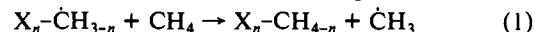
correlations were obtained with available kinetic data, one example of which is shown in Figure 1, and excellent correlations were obtained with thermodynamically based data, one example of which is shown in Figure 2.

More recently, extensive efforts have been made in the study of difunctionalized radicals. A special stabilizing effect in such systems was first suggested by Dewar.[6] Later, Katritzky suggested that radical centers substituted by an electron-acceptor *and* an electron-donor group should be especially stabilized, a concept termed *merostabilization*.[7] Still somewhat later, Viehe postulated that the combined action of an electron-releasing (*donor*) and an electron-withdrawing (*captor*) group on a radical center leads to an enhanced stabilization,[8] i.e., a greater stabilization than the sum of the stabilizations present in the singly substituted radicals. This concept has become known as the *captodative effect*, which has been recently reviewed.[9]

The basis for the proposed captodative effect has been described in terms of the relative numbers of resonance contributing structures that can be drawn for singly substituted radicals (two, as exemplified by the amino- and cyano-substituted radicals 1 and 2) versus that for the donor-acceptor substituted radical (five,

(1) For a comprehensive collection of discussions on substituent effects on the chemistry and properties of radicals, see: *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenyi, R., Eds.; NATO ASI Series C, Vol. 189; D. Reidel: Dordrecht, 1986.
(2) For references pertaining to monofunctional radicals, see the references cited in footnote 3.
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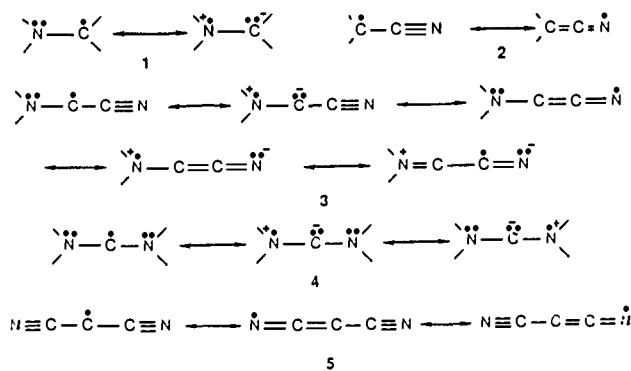
as exemplified by the aminocyano-substituted radical **3**).[9] The ability to write a greater number of resonance contributing structures for **3** relative to the sum for **1** and **2** was interpreted in terms of an expected enhanced stability for donor–acceptor substituted radicals such as **3**. For double-donor or double-acceptor substituted radicals such as **4** and **5** only three reasonable resonance contributing structures can be written. Accordingly, from this simple approach, systems such as **4** and **5** are expected to be destabilized relative to twice the stabilizations present in **1** and **2**.[9] A qualitative PMO theory explanation of the proposed captodative effect has also been forwarded.[9,10]

Support for the existence of the captodative effect has been claimed from the results of several studies. Captodatively substituted alkenes undergo particularly facile radical addition reactions[11] and (2 + 2) diradical-intermediate cycloaddition reactions.[12] Similarly substituted allenes also undergo particularly facile (2 + 2) cycloaddition reactions via diradical intermediates.[13] Slight captodative rate enhancement has also been claimed in the cyclization of 6-substituted 5-hexen-1-yl radicals.[14] Captodative rate accelerations have also been claimed in hydrogen atom abstraction reactions,[15] in the rearrangement reactions of substituted 2-arylmethylenecyclopropanes,[16] in the diastereomerization reactions of substituted cyclopropanes,[17] and in the thermal carbon–carbon bond homolysis of substituted 1,5-hexadienes[18] and bibenzyls.[19] ESR hyperfine coupling constant data have been used to evaluate the extent of spin delocalization in substituted radicals and related to the stabilization of the radical center by the attached substituents.[20] The ESR hyperfine coupling constant data for substituted benzyl radicals indicate that the presence of two acceptor or two donor groups results in decreased stabilization,
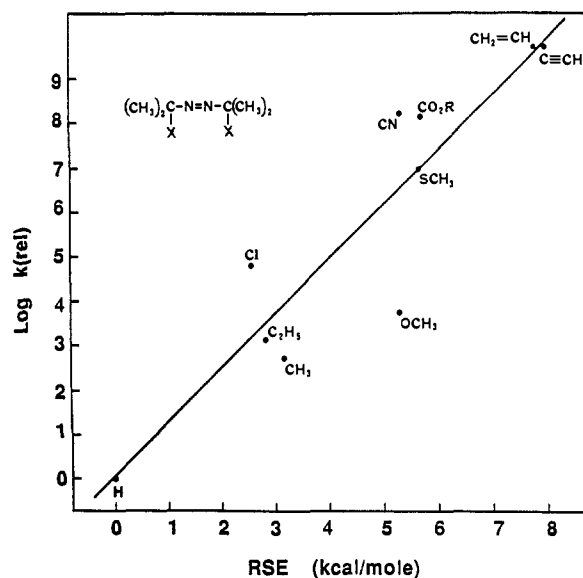

Figure 1. Plot of the logarithm of the relative rate constants for the thermolysis of 2-substituted azopropanes (Bandlish, B. K.; Garner, A. W.; Hodges, M. L.; Timberlake, J. W. *J. Am. Chem. Soc.* 1975, 97, 5856) versus substituted methyl radical RSE's.
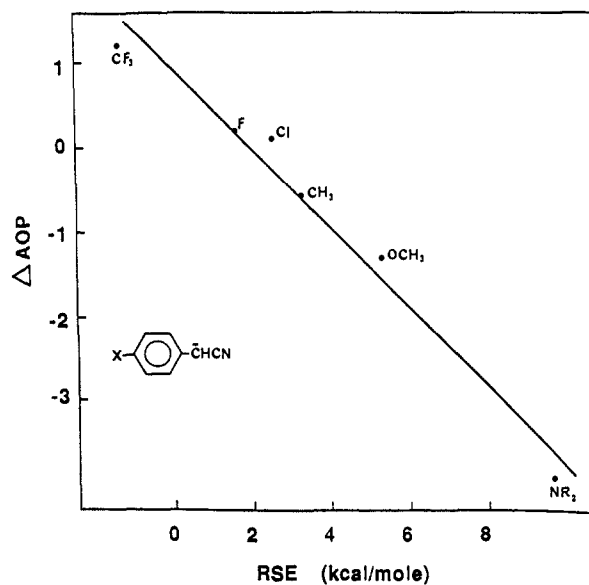

Figure 2. Plot of the ΔAOP (acidity oxidation potentials) derived from the reversible electrochemical oxidation of substituted phenylacetonitrile anions (Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* 1986, 108, 1979) versus substituted methyl radical RSE's.

whereas the presence of an acceptor and a donor group results in enhanced stabilization.[21] However, a comparison of the rotational barrier in the α-cyano-α-methoxybenzyl radical with the rotational barriers in the monosubstituted benzyl radicals indicates no special captodative stabilization that exceeds the additivity of the individual substituent effects.[22] The analysis of hyperfine coupling constant data and the measured rotation barriers for substituted allyl radicals is also claimed to support the existence of the captodative effect.[23] The values of the *E,Z* isomerization energy barriers for the substituted allyl radicals **6** are particularly striking. The sum of the lowerings in the isomerization barriers in the cyano- and methoxyallyl radicals (6.7 kcal/mol) is 3.0 kcal/mol *less* than the lowering in the isomerization barrier ob-

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served with the 1-cyano-1-methoxyallyl radical. This has been interpreted in terms of a captodative stabilization in the transition states for the isomerization reactions.[23]

6

Ea (kcal per mole)

|	
X = H, Y = D	15.7
X = H, Y = CN	10.2
X = H, Y = OCH₃	14.5
X = CN, Y = OCH₃	6.1
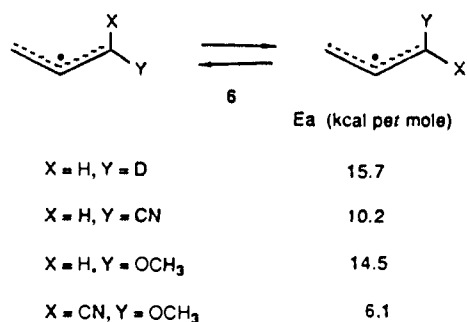
The rotation barriers about the C–N bonds in substituted aminoalkyl radicals are significantly greater when an acceptor group is present, indicative of extensive π-electron delocalization and captodative stabilization of the ground-state radicals.[24]

Theoretical studies have also suggested the existence of the captodative effect. Calculations at the UHF 4-31G level on the aminoborylmethyl and aminocyanomethyl radicals indicate significantly greater stabilization energies for the captodatively substituted radicals relative to the sums of the stabilization energies of the monosubstituted radicals.[25] Stabilization energies (SE's) have been calculated for a number of disubstituted radicals based on calculations carried out at the UHF 4-31G level.[26] Calculations have also been carried out on several C-centered radicals bearing both an acceptor and a donor group and on symmetrically substituted radicals at the UHF INDO level, the results of which indicate that the captodative radicals are significantly more stable than the corresponding symmetrical radicals in media of high dielectric constant, but *not* in the gas phase.[27] A recent experimental study, however, failed to detect any significant solvent polarity effect on the thermodynamic and kinetic parameters for the formation of α-cyan-α-methoxyalkyl radicals by homolytic dissociation of the respective dimers.[28] A relative radical stabilization (RRS/x) scale has been recently proposed based on data from the several different types of radical-forming reactions described above, which suggests that dicaptor-substituted radicals suffer destabilization and that captodatively substituted systems enjoy enhanced stabilization.[29]

Although the results of the studies outlined above provide support for the existence of the captodative effect, the results of some studies have indicated that there is no detectable extra stabilization in captodatively substituted radicals. The absolute rate constants for the dimerization of captodatively substituted methyl radicals in solution do not indicate that there is any kinetic stabilization present in such radicals.[30] An additive, and not a synergistic, effect has been observed in cyano- and methoxy-substituted radicals as deduced from the rates and activation parameters for the dissociation of substituted succinonitriles[31] and bibenzyls.[32] Finally, a study of the barriers of rotation in sub-

stituted benzyl radicals indicates that there is no special captodative stabilization that exceeds the additivity of the individual substituent effects.[22]

In a continuation of our theoretical studies on substituted radical systems, calculations have now been completed on a variety of disubstituted methyl radicals and methanes that allow for the calculation of RSE's for the disubstituted methyl radicals according to the isodesmic reaction shown in eq 2, the RSE being

$$X\text{--}\dot{C}H\text{--}Y + CH_4 \rightarrow X\text{--}CH_2\text{--}Y + \dot{C}H_3 \qquad (2)$$
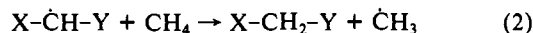
the change in total energy for the reaction. The differences between the RSE's calculated for eq 2 and the sum of the RSE's of the singly substituted methyl radicals[3] (ΔRSE's) will be a measure of the antagonistic or synergistic interactions of the substituents with the radical center.

Calculational Methods and Considerations. Prior calculations in the author's laboratories on the monosubstituted methyl radicals indicated that the UHF method is acceptable for calculations on open-shell systems containing two AO's in the delocalized π system of the radical (one on the carbon radical center and one on the substituent). The UHF wave functions for such systems are essentially those for the pure doublet states. For open-shell systems containing three or more AO's in the delocalized radical π system, however, the UHF wave function is significantly contaminated by higher spin-state wave functions. The contamination by higher spin-state wave functions lowers the calculated total energies of the species below that of the pure doublet state, resulting in artificially high RSE's. For example, the RSE calculated for the allyl radical at the UHF 4-31G level (⟨S⟩² value of 1.107 compared to 0.75 for a pure doublet state) is +22.14 kcal/mol.[3] This value is not in good agreement with experimentally derived estimates for the resonance or stabilization energy of the allyl radical of 10.2 and 11.4 kcal/mol from kinetic data on the gas-phase reactions of propene with iodine[33] and hydrogen iodide,[34] 11.7 kcal/mol from gas-phase equilibrium data for the dissociation-recombination reaction between 1,5-hexadiene and the allyl radical,[35] and 14.0–14.5 kcal/mol from kinetic data on the isomerization of the 1-deuterioallyl radical.[36] A very high level calculation on the allyl radical [GVB method with full CI using a (954/422) basis set supplemented by two additional π Gaussian functions on each carbon] gave a value for the "resonance" energy of 11.4 kcal/mol.[37] The use of better basis sets with the UHF method lowers the calculated RSE for the allyl radical (+20.59 kcal/mol at the fully geometry optimized 6-31G* level),[38] a value that is still unacceptably high. The inclusion of electron correlation gives significant improvement, giving values of +11.74, +12.89, +14.02, and +13.22 kcal/mol at the 6-31G* MP2, MP3, MP4SDO, and MP4SDTQ levels, respectively.[38] In a calculational effort of the magnitude required for this comprehensive study, calculations at this level are not feasible or realistic. As the principal problem appeared to be the higher spin-state contamination of the UHF wave function, the use of the ROHF method was explored.[3] The value of the RSE for the allyl radical calculated at the ROHF 4-31G level is +7.80 kcal/mol.[3] This value is lower than the experimentally based estimated values (undoubtedly due to the exclusion of spin polarization in the ROHF method), but does result in a value that gives an excellent correlation in a plot of RSE versus log *k*(rel) for the thermolysis of 2-substituted azopropanes (Figure 1). As a second example, the RSE calculated for the cyanomethyl radical at the UHF 4-31G level is +12.53 kcal/mol,[25] while that calculated at the ROHF 4-31G level is +5.34 kcal/mol, in excellent agreement with most

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of the experimentally based estimates that fall in the 5.0–5.5 kcal/mol range.[2]

The necessity for the inclusion of electron correlation corrections has also been evaluated. The inclusion of electron correlation at the MP2 level slightly increases (approximately 10% on the average) the values of the RSE's of those substituted radicals in which there is little change in geometry (principally bond lengths) on going from the radical to the substituted methane. In cases where large geometry changes occur, as in the case of the allyl radical, electron correlation is important. In the present study there are only small changes in geometry, and electron correlation correct calculations have not been carried out.

In view of the foregoing discussion, in the present study the calculations on the open-shell systems have been carried out at the ROHF 4-31G level with full geometry optimization using the GAMESS package of programs.[39] Calculations on the closed-shell systems have been carried out with the GAUSSIAN82 package of programs.[40] The RSE's are defined as the change in total energies for eq 2 and are not identical in definition with "resonance" energies. The author recognizes that the calculated values for the RSE's may not be in excellent agreement with experimentally determined "stabilization" or "resonance" energies; however, since all of the RSE's have been calculated at the same level and since geometrical changes between the substituted methyl radicals and methanes are relatively small, such differences between the best and the presently calculated values should be proportional, and a useful comparison and correlation should emerge.

In most of the systems incorporated in this study several conformations are possible for the substituted radicals and methanes, and an attempt has been made to locate all local minimum-energy structures (as indicated by the lack of a negative force constant). In most cases a conformation of a substituted radical can be directly related to a conformation of the substituted methane by a simple hydrogen atom abstraction process as would be encountered in a kinetically controlled process. Such atom abstraction processes have been shown to be highly conformationally dependent.[2] The RSE's calculated from conformationally related structures will be referred to as kinetic (K) RSE's. The RSE's relating the lowest energy conformations of the radical and the methane, which experimentally are virtually impossible to observe, will be referred to as thermodynamic (T) RSE's.

The total and SOMO energies of the substituted radicals are given in Table I. The total energies of the disubstituted methanes are given in Table II. The calculated RSE's and ΔRSE's are given in Table III. Although UHF 4-31G RSE's have been calculated for the singly substituted methyl radicals earlier, ROHF 4-31G RSE's for these systems have been calculated for consistency and are given in Table IV. The calculated geometrical parameters are provided in the tables appearing in the Supplementary Material. The Results and Discussion section is divided into subsections based on the type of π system present (i.e., ally. butadiene, or pentadienyl) and the number of electrons in the delocalized system.

Results and Discussion

Allyl-Type, One-Electron Delocalized Radical. Bisborylmethyl Radical (7). The bisborylmethyl radical is calculated to have the symmetrical, all-planar structure 7. Calculations on many possible conformations of bisborylmethane indicated that there appears to be only one local minimum structure, that being the C_s structure 8.
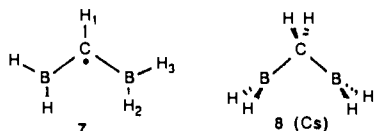
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Table I. ROHF 4-31G Total and SOMO Energies of Mono- and Disubstituted Methyl Radicals

radical		E_{tot}, au	E_{SOMO}, eV
methyl		-39.50179	-10.273
fluoromethyl		-138.22354	-11.306
hydroxymethyl		-114.24282	-9.839
aminomethyl		-94.45007	-8.154
borylmethyl		-64.72913	-10.831
bisborylmethyl	7	-89.94525	-11.213
borylfluoromethyl	9	-163.45777	-10.997
borylhydroxymethyl	11a	-139.48344	-9.490
borylhydroxymethyl	11b	-139.47891	-9.481
aminoborylmethyl	13	-119.69660	-7.809
difluoromethyl	15	-236.95719	-12.720
fluorohydroxymethyl	16a	-212.96792	-9.517
	16b	-212.96265	-9.463
aminofluoromethyl	18	-193.17120	-7.968
borylvinylmethyl	20a	-141.50772	-9.240
	20b	-141.51052	-9.260
borylethynylmethyl	22	-140.30309	-9.992
borylcyanomethyl	24	-156.32396	-11.588
fluorovinylmethyl	26a	-215.00944	-8.999
	26b	-215.00860	-9.019
hydroxyvinylmethyl	28a	-191.02703	-7.863
	28b	-191.02693	-7.915
	28c	-191.02692	-7.942
	28d	-191.02616	-7.797
aminovinylmethyl	30a	-171.23320	-6.444
	30b	-171.23388	-6.523
ethynylfluoromethyl	32	-213.79570	-9.989
ethynylhydroxymethyl	34a	-190.43199	-10.510
	34b	-190.43532	-10.761
cyanofluoromethyl	36	-229.81105	-11.531
cyanohydroxymethyl	38a	-205.83788	-10.052
	38b	-205.83648	-10.064
aminocyanomethyl	40	-186.05167	-8.371
fluoroformylmethyl	42a	-250.78397	-11.246
	43b	-250.77912	-11.203
hydroxyformylmethyl	44a	-226.81519	-9.661
	44b	-226.80301	-9.685
	44c	-226.80958	-9.745
	44d	-226.80668	-9.720
aminoformylmethyl	46a	-207.02830	-8.007
	46b	-207.02196	-8.077
divinylmethyl	48	-193.06472	-7.633
cyanovinylmethyl	50a	-207.87994	-9.548
	50b	-207.87984	-9.570
formylvinylmethyl	52a	-228.84517	-9.398
	52b	-228.84426	-9.310
	52c	-228.84249	-9.273
	52d	-228.84054	-9.460
diethynylmethyl	54	-190.64636	-9.124
cyanoethynylmethyl	56	-206.66682	-10.418
ethynylformylmethyl	58a	-227.63483	-10.207
	58b	-227.63211	-10.190
dicyanomethyl	60	-222.68132	-11.972
cyanoformylmethyl	62a	-243.65098	-11.778
	62b	-243.64885	-11.791
diformylmethyl	64	-264.61312	-11.621

The boryl group is calculated to be one of the most radical-stabilizing groups, having a RSE of +11.00 kcal/mol.[3] The RSE of 7 is calculated to be +13.74 kcal/mol, giving a value for ΔRSE of -8.26 kcal/mol, indicating substantial destabilization relative to twice the RSE of the borylmethyl radical of +11.71 kcal/mol. This is easily understood on the basis of simple PMO theory in that the interaction of the lower lying SOMO of the methyl radical with the vacant orbital of the first boryl group substantially lowers the energy of the SOMO in the borylmethyl radical. On introduction of the second boryl group, a larger energy gap exists between the SOMO of the borylmethyl radical and the vacant orbital of the second boryl group, resulting in a smaller interaction energy on going from the boryl- to the bisborylmethyl radical.
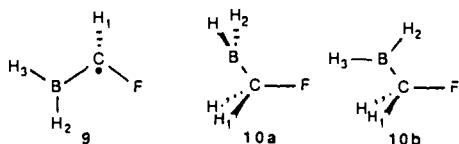
Allyl-Type, Three-Electron Delocalized Radicals. Borylfluoromethyl Radical (9). The borylfluoromethyl radical is calculated to have the slightly nonplanar structure 9. Two mini-

Table II. 4-31G Optimized Total Energies of Disubstituted Methanes

structure		E_{tot}, au
bisborylmethane	8	-90.56133
borylfluoromethane	10a	-164.06065
	10b	-164.06960
borylhydroxymethane	12a	-140.07568
	12b	-140.08117
	12c	-140.06777
	12d	-140.08014
aminoborylmethane	14a	-120.29214
	14b	-120.28043
difluoromethane		-237.59322^a
fluorohydroxymethane	17a	-213.60192
	17b	-213.61222
aminofluoromethane	19a	-193.81767
3-boryl-1-propene	21a	-142.10837
	21b	-142.11081
	21c	-142.10572
	21d	-142.11023
	21e	-142.11251
	21f	-142.11345
3-boryl-1-propyne	23a	-140.90857
	23b	-140.91023
borylacetonitrile	25a	-156.93456
	25b	-156.93826
3-fluoro-1-propene	27a	-215.63183
	27b	-215.63308
3-hydroxy-1-propene	29a	-191.64370
	29b	-191.64151
	29c	-191.64211
	29d	-191.64340
3-amino-1-propene	31a	-171.84123
	31b	-171.83786
	31c	-171.84078
3-fluoro-1-propyne	33	-214.42052
3-hydroxy-1-propyne	35a	-189.81848
	35b	-189.81563
fluoroacetonitrile	37	-230.43954
hydroxyacetonitrile	39a	-206.45512
	39b	-206.45781
aminoacetonitrile	41	-186.66298
fluoroacetaldehyde	43a	-251.40790
	43b	-251.40173
hydroxyacetaldehyde	45a	-227.42414
	45b	-227.41508
	45c	-227.42338
	45d	-227.41614
aminoacetaldehyde	47a	-207.62261
	47b	-207.62445
	47c	-207.62413
	47d	-207.62325
1,4-pentadiene	49a	-193.67145
	49b	-193.67032
3-cyanopropene	51a	-208.49262
	51b	-208.49251
3-butenal	53a	-229.45286
	53b	-229.45247
1,4-pentadiyne	55	-191.25773
3-cyano-1-propyne	57	-207.28201
3-butynal	59a	-228.24710
	59b	-229.24470
dicyanomethane	61	-223.30150
cyanoacetaldehyde	63a	-244.26924
	63b	-244.26764
diformylmethane	65	-265.22763

^a Reference 3.

Table III. RSE's and ΔRSE's (kcal/mol) of the Disubstituted Methyl Radical Systems

radical		RSE	ΔRSE
Three 2p AO, One Electron System			
CH(BH₂)₂	7	+13.74	-9.68
Three 2p AO, Three Electron Systems			
FCHBH₂	9 → 10b; K, T	+16.41	+2.87
HOCHBH₂	11b → 12b; K	+22.41	+4.88
	11a → 12a; K	+25.90	+8.37
	11a → 12b; T	+23.06	+5.53
H₂NCHBH₂	13 → 14b; K	+33.98	+11.99
	13 → 14a; T	+26.63	+4.64
Three 2p AO, Five Electron Systems			
F₂CH		+1.22	-2.44
HOCHF	16b → 17a; K	-0.81	-8.46
	16a → 17b; K, T	-3.97	-11.62
H₂NCHF	18 → 19a, T	+5.33	-6.78
Four 2p AO, Three Electron Systems			
H₂BCHCH=CH₂	20a → 21b; K	+21.89	+2.38
	20a → 21a; K	+23.42	+3.91
	20b → 21d; K	+24.01	+4.50
	20b → 21c; K	+22.58	+3.07
	20b → 21f; T	+21.99	+2.48
H₂BCHC≡CH	22 → 23b; K, T	+19.35	-0.36
	22 → 23a; K	+20.39	+0.68
H₂BCHC≡N	24 → 25b; K,T	+14.96	-2.19
	24 → 25a; K	+17.18	+0.13
Four 2p AO, Five Electron Systems			
FCHCH=CH₂	26a → 27a; K	+9.78	+0.15
	26b → 27b; K	+8.47	-1.15
	26b → 27a; T	+8.99	-0.63
HOCHCH=CH₂	28a → 29c; K	+14.37	+0.75
	28b → 29d; K	+13.52	-0.10
	28c → 29c; K	+14.30	+0.68
	28d → 29a; K	+12.83	-0.79
	28e → 29a; T	+13.37	-0.25
H₂NCHCH=CH₂	30a → 31b; K	+20.91	+2.83
	30a → 31a; K	+18.79	+0.71
	30b → 31c; K	+19.50	+1.42
	30b → 31a; T	+19.22	+1.14
FCHC≡CH	32 → 33; K,T	+8.26	-0.57
HOCHC≡CH	34a → 35a; K,T	+13.26	-0.56
	34b → 35b; K	+13.57	-0.25
FCHC≡N	36 → 37	+5.95	-1.22
HOCHC≡N	38a → 39b; K,T	+11.33	-1.67
	38b → 39a; K	+12.14	-0.86
H₂NCHC≡N	40 + 41	+16.73	+1.11
FCHCHO	42a → 43a; K,T	+8.82	-0.67
	42b → 43b; K	+9.64	+0.15
HOCHCHO	44a → 45a; K,T	+18.22	+4.74
	44b → 45b; K	+16.26	+2.78
	44c → 45c; K	+15.17	+1.69
	44d → 45d; K	+17.90	+4.42
H₂NCHCHO	46a → 47a; K	+27.40	+9.46
	46b → 47c; K	+22.47	+4.53
	46a → 47b; T	+26.25	+8.31
Five 2p AO, Five Electron Systems			
H₂C=CHCHCH=CH₂	48a → 49b; K,T	+20.32	+4.72
	48a → 49a; T	+19.61	+4.01
N≡CCHCH=CH₂	50b → 51a; K	+15.81	+2.67
	50a → 51b; K	+15.94	+2.80
	50a + 51a; T	+15.87	+2.73
OCHCHCH=CH₂	52a → 53a; K,T	+19.01	+3.55
	52b → 53b; K	+18.68	+3.22
(HC≡C)₂CH	54 → 55; K,T	+16.70	+0.70
N≡CCHC≡CH	56 → 57; K,T	+14.30	+0.96
OCHCHC≡CH	58a → 59a; K,T	+16.13	+0.47
	58b → 59b; K	+15.93	+0.27
N≡CCHC≡N	60 → 61	+11.17	+0.49
OCHCHC≡N	62a → 63a; K,T	+12.35	-0.65
	62b → 63b; K	+12.04	-0.95
OCHCHCHO	64 → 65	+14.73	-0.59

mum-energy conformations have been located for borylfluoromethane, **10a** and **10b**, with the latter being lower in energy by

5.62 kcal/mol. It is interesting to note that in **10a** the B-C-F

angle is calculated to be 100.07°, considerably less that expected for tetrahedral geometry about carbon, indicating an attractive

**Table IV.** ROHF 4-31G RSE's of Monosubstituted Methyl Radicals

radical	RSE (kcal/mol)	radical	RSE (kcal/mol)
H_2BCH_2	+11.71	$H_2C=CHCH_2$	+7.80
FCH_2	+1.83	$HC\equiv CCH_2$	+8.00
$HOCH_2$	+5.82	$HCOCH_2$	+7.66
H_2NCH_2	+10.28	$N\equiv CCH_2$	+5.34

long-range interaction between a nonbonding pair of electrons on fluorine and the vacant orbital on boron.

The ΔRSE relating **9** to **10a** (both the kinetic and thermodynamic ΔRSE) is calculated to be +2.87 kcal/mol, representing a slight extra stabilization, or captodative effect.

Borylhydroxymethyl Radical (11). Calculations on the borylhydroxymethyl radical indicated the existence of two essentially all-planar conformations **11a** and **11b**, with the former being lower in energy by 2.84 kcal/mol. Four minimum energy conformations have been located for borylhydroxymethane (**12a–d**). In **12a** the
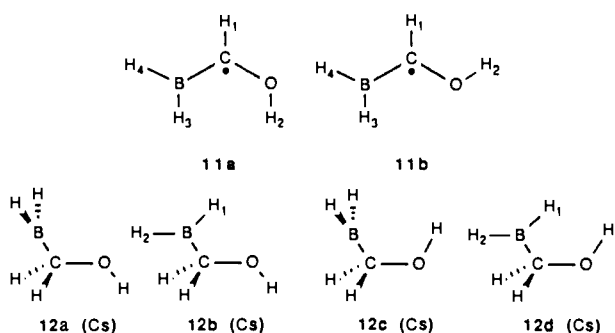
B-C-O angle is 97.85°, less than that in the borylfluoromethane conformation **12a**, suggesting a stronger attractive interaction between boron and oxygen. Of the conformations for **12, 12b** is lowest in energy followed by **12d** (+0.65 kcal/mol), **12a** (+3.44 kcal/mol), and **12c** (+8.40 kcal/mol).

In this system the kinetic ΔRSE's relating **11b** with **12b** and **11a** with **12b** are +4.88 and +8.37 kcal/mol, respectively, while the thermodynamic ΔRSE relating **11a** with **12b** is +5.53 kcal/mol. These ΔRSE values indicate the presence of a significant extra stabilization, or captodative effect.

Aminoborylmethyl Radical (13). Calculations have been carried out previously on **13** and the corresponding monosubstituted methyl radicals at the UHF 4-31G level with full geometry optimization.[25] The UHF-based RSE's (kcal/mol) for the radicals are as follows: BH_2CHNH_2, 33.4; NH_2CH_2, 10.2; BH_2CH_2, 10.9.[25] The resulting ΔRSE for **13** was calculated to be +12.3 kcal/mol.[25]

In this study calculations at the ROHF 4-31G level indicate that **13** exists in an essentially all-planar structure. Two minimum-energy structures were located for aminoborylmethane, one having the azaboracyclopropane structure **14a**. In **14a** the B-C-N
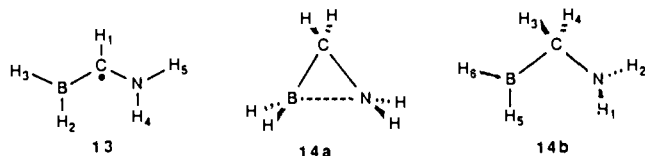

angle is calculated to be 66.17°, with a B-N distance of 1.687 Å. In this series of substituted borylmethanes there is a progressively stronger interaction between the nonbonded pair of electrons on the heteroatom and the vacant orbital on boron in going from fluorine to oxygen to nitrogen. The azaboracyclopropane structure **14a** is calculated to be *lower* in energy than **14b** by 7.35 kcal/mol!

The RSE relating **13** with **14b**, which might be considered to be the kinetic RSE, is +33.98 kcal/mol, with a ΔRSE or +11.99 kcal/mol. For the thermodynamically controlled relationship between **13** and **14a** both the RSE and ΔRSE are considerably

lower, being +26.63 and +4.64 kcal/mol, respectively. The values of the ΔRSE's indicate the presence of a very substantial extra stabilization in **13**.

All members of this series of substituted borylmethyl radicals are predicted to possess extra stabilization, consistent with the captodative concept for acceptor–donor substituted radicals. The ΔRSE's increase on going from fluorine to oxygen to nitrogen. This is as expected in that the energy gaps between the lower lying nonbonded pair orbitals on the heteroatoms and the higher lying SOMO of the borylmethyl radical decrease in the sequence fluorine to oxygen to nitrogen, resulting in increasing interaction energies and greater net one-electron stabilization.[41] In this sequence there is also a decrease in the electronegativity of the heteroatom, which results in less destabilization of the radical center.[3]

Allyl-Type, Five-Electron Delocalized Radicals. Difluoromethyl Radical (15). The RSE of **15** calculated at the UHF 4-31G level is +0.56 kcal/mol.[3] At the ROHF 4-31G level the RSE of **15**
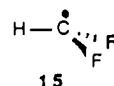

is calculated to be +1.22 kcal/mol, with a value for the ΔRSE of -2.44 kcal/mol. The difluoromethyl radical suffers net destabilization relative to twice the stabilization afforded by a single fluorine atom of 1.83 kcal/mol.

Fluorohydroxymethyl Radical (16). The fluorohydroxymethyl radical is calculated to exist in the two all-planar conformations **16a** and **16b**, with the former being lower in energy by 3.31 kcal/mol. Two conformations were located for fluorohydroxymethane, **17a** and **17b**, with the latter being lower in energy by 6.46 kcal/mol.
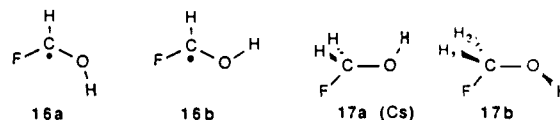
The kinetic RSE relating **16b** with **17a** is -0.81 kcal/mol. The kinetic and thermodynamic RSE relating **16a** with **17b** is -3.97 kcal/mol. In both relationships the fluorohydroxymethyl radical suffers *destabilization* relative to the methyl radical. The ΔRSE relating **16a** with **17b** is -11.62 kcal/mol, indicating a very substantial extra destabilization of the radical center by the combination of the fluoro and hydroxy groups.

Aminofluoromethyl Radical (18). The aminofluoromethyl radical is calculated to exist as the all-planar structure **18**. Of
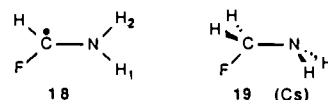

the two possible staggered conformations available to aminofluoromethane, only **19** with the nonbonding pair of electrons on nitrogen being antiperiplanar to the fluorine represents a minimum-energy structure. The RSE is +5.33 kcal/mol, which gives a ΔRSE of -6.78 kcal/mol, indicating a very substantial net destabilization of the radical center by the combination of the amino and fluoro functional groups.

Summary of the Allyl-Type Delocalized Radical Systems. The MO's of the allyl-type delocalized radicals resemble the MO's of the allyl system with one low-lying all-bonding π MO, an intermediate-lying MO of the nonbonding type, and a high-lying antibonding MO. In the diacceptor radical **7** there is a single electron present, which occupies the bonding MO, leading to a substantial stabilization of the radical center. The ΔRSE, however, is negative, indicating a net destabilization relative to twice the RSE of the borylmethyl radical for the reasons indicated earlier. In the three-electron systems **9, 11,** and **13** the lowest lying bonding MO is doubly occupied and the nonbonding-type MO is singly

(41) Pasto, D. J. *Tetrahedron Lett.* **1986**, *27*, 2941.

occupied. In these systems there is net two-electron stabilization with one electron occupying the nonbonding MO, which overall results in net *extra* stabilization in these systems relative to the sum of the RSE's of the singly substituted radicals. In the five-electron systems **15**, **16**, and **18** the lowest lying bonding and the nonbodning MO's are doubly occupied with one electron occupying the antibonding MO. This occupancy results in destabilization, which is further enhanced by increased π-space electron repulsion and σ inductive destabilization,[3] the overall effect producing substantial net destabilization of the radical center relative to the sum of the stabilizations present in the singly substituted radicals.

Butadiene-Type, Three-Electron Delocalized Radicals. Borylvinylmethyl Radical (20). Calculations on the borylvinylmethyl radical[42] indicate the existence of the two all-planar structures **20a** and **20b**, with the *E* conformation **20b** being lower in energy
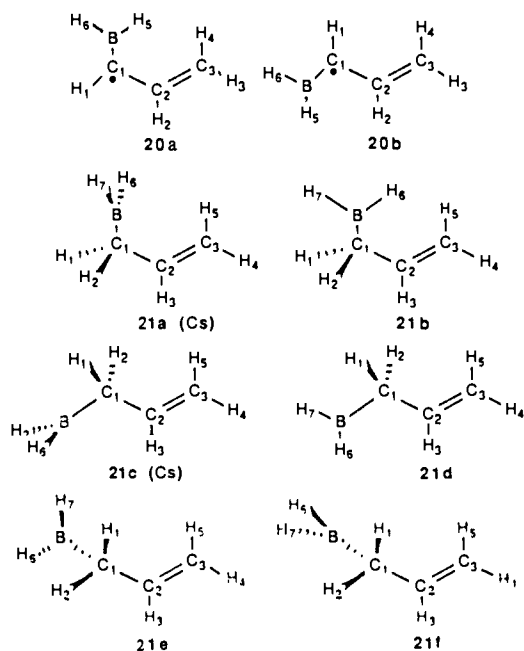
by 1.76 kcal/mol. Six minimum-energy conformations have been located for allylborane (**21a–f**). Conformation **21f** is lowest in energy, followed in sequence by **21e** (+0.59 kcal/mol), **21b** (+1.66), **21d** (+2.02), **21a** (+3.19), and **21c** (+4.85). Least motion hydrogen atom abstraction processes relate **20a** with **21b** and **20b** with **21d**, with RSE's of +21.89 and +24.01 kcal/mol and ΔRSE's of +2.38 and +4.50 kcal/mol. Kinetic processes

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(42) In contrast to the symmetrical structure of the allyl radical, these calculations indicate that in all of the substituted allyl radicals there is very extensive bond localization in the "allyl" portions of the radicals. For example, the C_1–C_2 bond lengths in **20a** and **20b** are calculated to be 1.447 and 1.441 Å, respectively, with the C_2–C_3 bond lengths both being 1.331 Å. Similar bond localization in substituted allyl radicals has been noted previously.[35] Bond localization is expected based on a simple PMO approach in that the three fragments comprising the substituted allyl radicals, i.e., the functional group, the methyl radical, and the vinyl group, possess substantially different π MO energies, which on mixing of the group π MO wave functions will produce delocalized MOs in which the individual MOs will contain dominant contributions from the closest lying fragment MO. Accordingly, in this article the substituted allyl radicals are more appropriately referred to as substituted-vinylmethyl radicals.

(43) In the heteroatom-substituted vinylmethyl (allyl) radicals there is a net attractive long-range interaction between the 2p AO on the heteroatom with the 2p AO of C_3 due to the added long-range attractive interaction in the butadiene-type Ψ_3 SOMO.

(44) The preference for **34b** over **34a** appears to be due to a stabilizing long-range hydrogen-bonding interaction between the O–H with the in-plane π MO of the triple bond. This is in contrast to the preferred conformations with the hydroxyvinylmethyl (hydroxyallyl) radical in which the O–H prefers to be oriented antiperiplanar to the C=C. Long-range hydrogen bonding also appears to be the reason that **35a** is lower in energy than **35b**.

(45) Sustmann, R. *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenyi, R., Eds.; NATO ASI Series C, Vol. 189; D. Reidel: Dordrecht, 1986; pp 143–166.

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relating **20a** with **21a** and **20b** with **21c** require rotation of the plane of the BH$_2$ group. The RSE's for these two relationships are +23.42 and +22.58 kcal/mol, with ΔRSE's of +3.91 and +3.07 kcal/mol. No simple kinetic process relates either of the radicals with **21e** and **21f**. The thermodynamically controlled process relates **20b** with **21f**, which has a RSE of +21.99 kcal/mol and a ΔRSE of +2.48 kcal/mol. The presence of both a boryl and vinyl group at a radical center results in extra stabilization over the sum of the stabilizations provided by the individual groups. This would only be consistent with the captodative effect theory if one considers the vinyl group to be the donor functional group.

Borylethynylmethyl Radical (22). Calculations on the borylethynylmethyl radical indicate the existence of a single minimum-energy, all-planar structure **22**. Only two minimum-energy
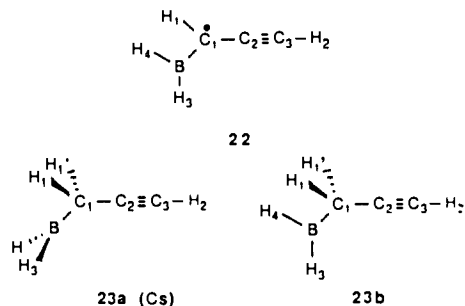
conformations were located for 3-boryl-1-propyne, one having the BH$_2$ group perpendicular to the C_1C_2 bond and the other having the BH bond eclipsed with the C_1C_2 bond, with the latter being lower in energy by 1.04 kcal/mol.

The least motion kinetic and thermodynamic processes relate **22** with **23a** with a RSE of +19.35 kcal/mol and a ΔRSE of –0.36 kcal/mol. The negative ΔRSE value of –0.36 kcal/mol indicates a slight destabilization of the disubstituted radical relative to the sum of the stabilizations in the singly substituted radicals. In this case the ethynyl group appears to be acting as an acceptor, in contrast to the vinyl group, which appeared to be acting as a donor group.

Borylcyanomethyl Radical (24). The borylcyanomethyl radical is calculated to exist as the all-planar structure **24**. Similar to
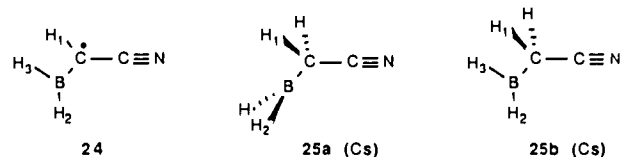

23, only two minimum-energy conformations were located, one having the BH$_2$ oriented perpendicular to the nitrile function (**25a**) and one having a BH bond eclipsed with the C–C bond, with the latter being lower in energy by 2.32 kcal/mol.

The least motion, kinetically controlled hydrogen atom abstraction process, as well as the thermodynamically controlled process, relates **24** with **25b** with a RSE of +14.96 kcal/mol and a ΔRSE of –2.19 kcal/mol. In this case **25b** suffers net destabilization relative to the sum of the stabilizations provided a radical center by the boryl and cyano groups.

In this series of butadiene-type, three-electron delocalized radicals there is an obvious decrease in the stabilization of the radical center as the electronegativity of the π function increases. The extra stabilization calculated to be present in the vinyl-substituted borylmethyl radical decreases on going to the more electronegative ethynyl and cyano groups, the presence of these groups resulting in net destabilization.

Butadiene-Type, Five-Electron Delocalized Radicals. Fluorovinylmethyl Radical (26). Calculations on the fluorovinylmethyl radical indicate the existence of two all-planar structures **26a** and **26b**, with the *Z* isomer **26a** being lower in energy by 0.53 kcal/mol.[36] Calculations on 3-fluoro-1-propene located only two minimum-energy conformations **27a** and **27b**, with the latter being lower in energy by 0.78 kcal/mol. The ΔRSE for the least motion kinetic process relating **26a** with **27a** is +0.15 kcal/mol, indicating
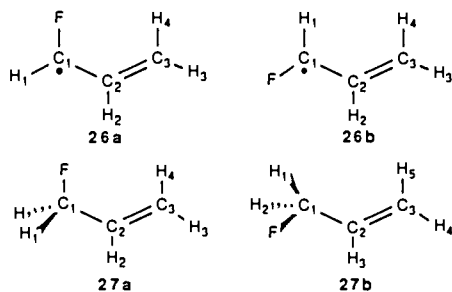
the presence of a very slight extra stabilization in **26a**. The thermodynamic ΔRSE relating **26a** with **27a** is –0.63 kcal/mol, indicating a slight net destabilization.

Hydroxyvinylmethyl (Hydroxyallyl) Radical (28). Calculations of the hydroxyvinylmethyl radical indicate the existence of four, all-planar conformations (**28a–d**). Structure **28a** is lowest in
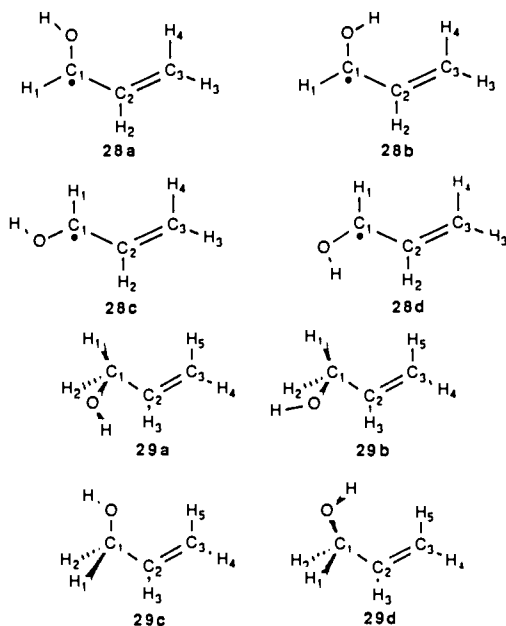
energy, followed by **28b** (+0.06 kcal/mol), **28c** (+0.07 kcal/mol), and **28d** (+0.55 kcal/mol). Four minimum-energy structures were located for 3-hydroxy-1-propene (allyl alcohol) (**29a–d**). Conformation **29a** is lowest in energy, followed by **29b** (+0.19 kcal/mol), **29c** (+1.00 kcal/mol), and **29d** (+1.37 kcal/mol). The ΔRSE's are very conformationally dependent. The ΔRSE's for the kinetic processes relating **28a** with **29c**, **28b** with **29d**, **28c** with **29c**, and **28d** with **29d** are +0.75, –0.10, +0.68, and –0.79 kcal/mol, respectively. The thermodynamic ΔRSE relating **28e** with **29a** is –0.25 kcal/mol, indicating the presence of a slight destabilizing effect.

Aminovinylmethyl Radical (Aminoallyl Radical) (30). Calculations on the aminovinylmethyl radical indicate that the radical exists in the two all-planar conformations **30a** and **30b**, with the
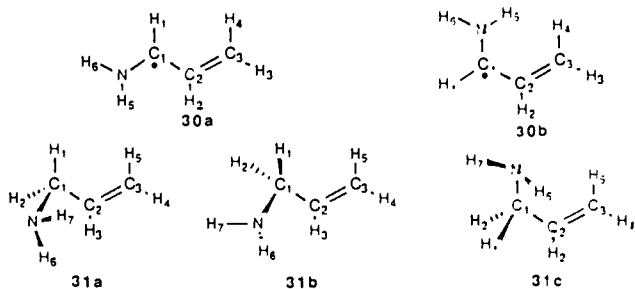

latter being lower in energy by 0.43 kcal/mol. Three minimum-energy conformations were located for 3-amino-1-propene (allylamine) (**31a–c**). The ΔRSE calculated for the kinetic processes relating **30a** with **31c**, **30a** with **31a**, and **30b** with **31b** are +2.83,

+0.71, and +1.42, respectively, all indicating the presence of extra stabilization over the sum of the stabilizations afforded the radical center by the individual functions. The thermodynamic ΔRSE relating **30b** with **31a** is +1.14 kcal/mol, indicating the presence of a slight extra stabilizing effect.

In this series of substituted vinylmethyl (allyl) radicals the presence of the highly electronegative fluorine atom results in net destabilization. The decrease in the electronegativity of the group attached to the vinylmethyl radical on going from fluorine to oxygen and then to nitrogen results in increased extra stabilization of the radical center.

Fluoroethynylmethyl Radical (32). The fluoroethynylmethyl radical is calculated to have the all-planar structure **32**. The
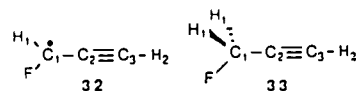

ΔRSE calculated for **32** is –0.57 kcal/mol, indicating a slight destabilization of the radical compared to the sum of the stabilization energies of the fluoromethyl and propargyl radicals. This value is comparable to that calculated for the fluorovinylmethyl radical.

Hydroxyethynylmethyl Radical (34). Calculations on the hydroxyethynylmethyl radical indicate the existence of two, all-planar, minimum-energy conformations **34a** and **34b**, with the
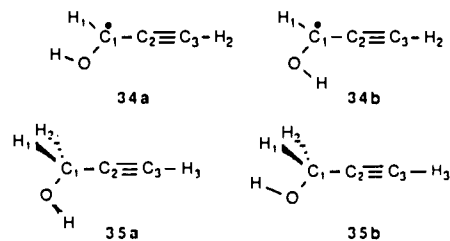
latter being lower in energy by 1.79 kcal/mol.[37] Of the two conformations located for 3-hydroxy-1-propyne (propargyl alcohol), conformation **35a** is lower in energy than **35b** by 2.09 kcal/mol. The calculated ΔRSE for the kinetic and thermodynamic processes relating **34a** with **35a** is –0.56 kcal/mol, while the ΔRSE for the kinetic process relating **34a** with **35b** is –0.25 kcal/mol. These ΔRSE values indicate slight net destabilization to be present in the disubstituted radical compared to the sum of the stabilizations present in the singly substituted methyl radicals, which is slightly greater than that calculated for the hydroxyvinylmethyl radical. This would appear to be due to the slightly more electronegative nature of the ethynyl group compared to the vinyl group.

Cyanofluoromethyl Radical (36). Calculations have been previously carried out on **36** at the UHF 4-31G level, giving a total energy of –229.82688 au with a calculated value for the RSE of +13.90 kcal/mol.[26a] The present calculations carried out at
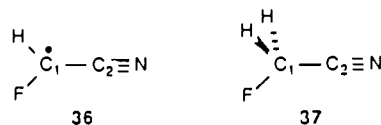

the ROHF 4-31G level give a total energy of –299.81105 au, with a value for the RSE of +5.95 kcal/mol. The value for the ΔRSE is –1.22 kcal/mol, indicating net destabilization. In this case fluorine must be considered to be the donor and the cyano function the acceptor, which, according to the captodative effect concept, should result in enhanced stabilization. The presence of two highly electronegative groups on the radical center apparently results in destabilization of this system.

Cyanohydroxymethyl Radical (38). Calculations have been previously carried out on **38** (the conformation about the C–O bond was not specified) at the UHF 4-31G level, giving a total energy of –205.85235 au and a RSE of +18.41 kcal/mol.[26a] Calculations in this study indicate that **38** exists in the two con-

formations **38a** (-205.83788 au) and **38b**, with the former being

38a   38b

39a (Cs)   39b
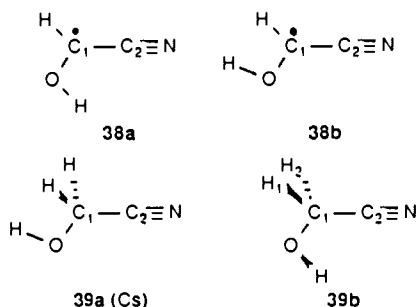
lower in energy by 0.88 kcal/mol. Two conformations were located for hydroxyacetonitrile, **39a** and **39b**, with the latter being lower in energy by 1.69 kcal/mol. The kinetic and thermodynamic ΔRSE relating **38a** with **39b** is -1.67 kcal/mol, while the kinetic ΔRSE relating **38b** with **39a** is -0.86 kcal/mol. These ΔRSE's indicate net destabilization relative to the sum of the stabilizations in the singly substituted radicals. This is not consistent with the captodative concept, which suggests that this donor–acceptor substituted system should enjoy extra stabilization.

In view of this result and the question of the effect of using the ROHF method instead of the UHF method, calculations have also been carried out on this system at the fully geometry optimized UHF and HF 6-31G* level. At this level the RSE's for the cyanomethyl, hydroxymethyl, and **38a** are calculated to be +9.75, +5.97, and +15.54 kcal/mol, respectively. The ΔRSE for the process relating **38a** with **39b** is -0.18 kcal/mol. Thus, the results of both ROHF and UHF calculations are in agreement that *38a*, although being a captodative system, does not enjoy extra stabilization, but in fact suffers slight destabilization. This result is consistent with the conclusion that the *tert*-butoxycyanomethyl radical is not kinetically stabilized toward dimerization[30] and the conclusion from rotational barrier measurements of substituted benzyl radicals that there is no special captodative stabilization present in the α-cyano-α-methoxybenzyl radical.[22] This requires a reinterpretation of the unusually low energy barrier observed for the isomerization of the 1-cyano-1-methoxyallyl radical.

Aminocyanomethyl Radical (40). Calculations have been previously carried out on **40** at the UHF 4-31G level, giving a

40   41 (Cs)
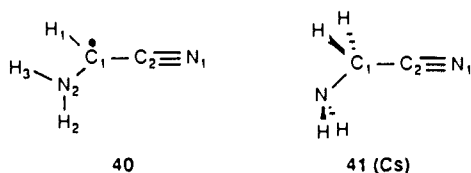
total energy of -186.06397 au[25,26] with a RSE of +22.46 kcal/mol.[26a] The presently calculated total energy is -186.05167 au with a RSE of +16.73 kcal/mol. The only apparent minimum-energy conformation for aminoacetonitrile is that shown as structure **41**. The ΔRSE calculated for **40** is +1.11 kcal/mol, indicating slight extra stabilization relative to the sum of the RSE's of the singly substituted methyl radicals.

In this series of captodatively substituted cyanomethyl radicals the fluoro- and hydroxy-substituted cyanomethyl radicals are predicted to suffer slight captodative destabilization, while the amino-substituted radical enjoys slight captodative stabilization. This trend suggests that inductive effects are dominant, the more electronegative fluoro and hydroxy groups inductively destabilizing the radicals, while the less electronegative amino group allows for some captodative stabilization.

Fluoroformylmethyl Radical (42). The fluoroformylmethyl radical exists in the two conformations **42a** and **42b**, with the former being lower in energy by 3.04 kcal/mol. Only two minimum-energy conformations were located for fluoroacetaldehyde, those having the fluorine oriented syn- and antiperiplanar to the carbonyl group (**43a** and **43b**), with the antiperiplanar conformation being lower in energy by 3.87 kcal/mol. The kinetic and thermodynamic ΔRSE relating **42a** with **43a** is -0.67

42a   42b   43a (Cs)   43b (Cs)
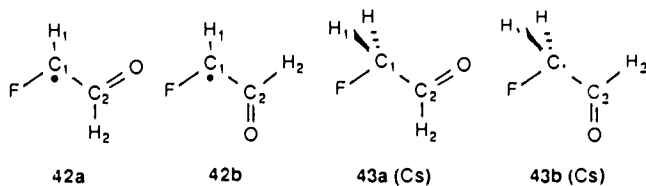
kcal/mol, indicating slight net destabilization. The ΔRSE for the kinetic process relating **42b** with **43b** is +0.15 kcal/mol, indicating a very slight extra stabilization. In this system stabilization or destabilization is a sensitive function of conformation.

Formylhydroxymethyl Radical (44). Four all-planar minimum-energy conformations have been located for the formyl-hydroxymethyl radical (**44a-d**). Of these, **44a** is lowest in energy,

44a   44b

44c   44d

45a (Cs)   45b (Cs)


45c (Cs)   45d (Cs)
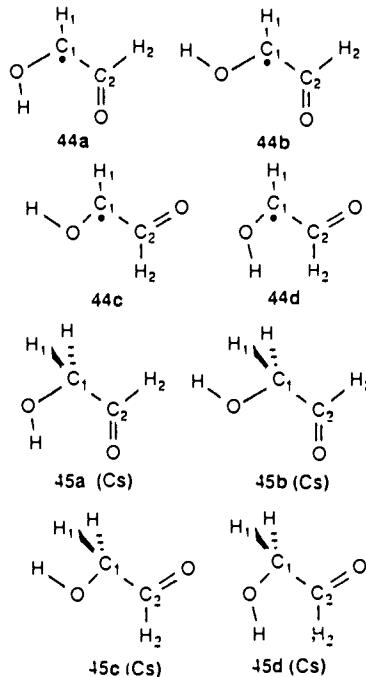
followed by **44c** (+3.52 kcal/mol), **44d** (+5.34 kcal/mol), and **44b** (+7.64 kcal/mol). Four minimum-energy conformations have also been located for hydroxyacetaldehyde (**45a-d**). No local minima were found having a C-H bond syn- or antiperiplanar to the carbonyl group. Of these four conformations, **45a** is lowest in energy, followed by **45c** (+0.48 kcal/mol), **45d** (+5.02 kcal/mol), and **45b** (+5.67 kcal/mol). The kinetic and thermodynamic ΔRSE relating **44a** with **45a** is +4.74 kcal/mol, while the ΔRSE's for the kinetic processes relating **44b** with **45b**, **44c** with **45c**, and **44d** with **45d** are +2.78, +1.69, and +4.42 kcal/mol, respectively. All of these ΔRSE's indicate the presence of extra stabilization relative to the sum of the RSE's of the singly substituted methyl radicals.

Aminoformylmethyl Radical (46). The aminoformylmethyl radical exists in the all-planar conformations **46a** and **46b**, with the former being 3.97 kcal/mol lower in energy. Four minimum-energy conformations have been located for aminoacet-aldehyde (**47a-d**). Of these, **47b** is lowest in energy, followed by **47c** (+0.09 kcal/mol), **47d** (+0.75 kcal/mol), and **47a** (+1.15 kcal/mol). The ΔRSE's for the kinetic processes relating **46a** with **47a** and **46b** with **47c** are +9.46 and +4.53 kcal/mol. The thermodynamic ΔRSE relating **46a** with **47b** is +8.31 kcal/mol. All of these ΔRSE's indicate the presence of significant captodative stabilization.

In this sequence of substituted formylmethyl radicals, the fluoro-substituted radical is indicated to be neither significantly stabilized nor destabilized. On going to the less electronegative hydroxy and amino substituents, significant captodative stabilization is indicated to be present.

Summary of the Butadiene-Type Delocalized Radical Systems. In the three-electron (diacceptor) systems, the borylvinylmethyl
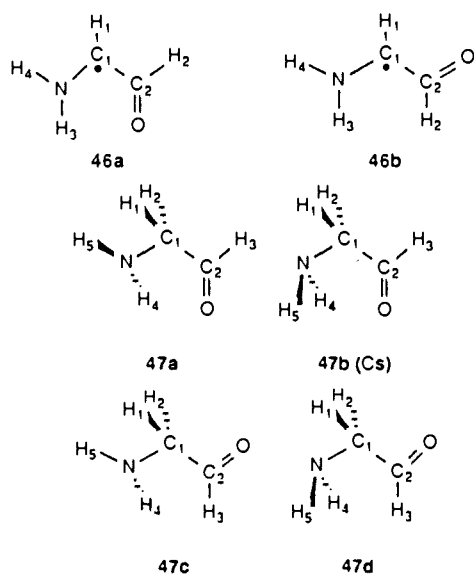
radical is predicted to possess significant extra stabilization, contrary to the captodative concept. As the electronegativity of the π acceptor increases, the extra stabilization decreases, becoming destabilizing in the borylcyanomethyl radical, which is consistent with the captodative concept. In the five-electron (acceptor–donor) systems, whether the radical enjoys extra stabilization or suffers destabilization is a sensitive function of the electronegativity of the acceptor and donor groups. The more electronegative the donor group, the less is the stabilization afforded the radical center. The more electronegative the acceptor group, the greater is the stabilization afforded the radical center. It is obvious that whether or not the captodative effect will be seen will be highly dependent on the nature of the attached groups and that the captodative effect is *not* expected to be present in all acceptor–donor substituted radical systems.

There is a further interesting point to make on comparing the three- with the five-electron systems. The three-electron systems seem to enjoy a greater degree of stabilization than do the five-electron systems. This can be understood on the basis of a simple MO approach. In the three-electron systems Ψ_1 is doubly occupied, with the SOMO being the bonding Ψ_2, butadiene-type MO. In the five-electron systems, Ψ_1 and Ψ_2 are doubly occupied, with the SOMO being the antibonding butadiene-type MO Ψ_3. The occupancy of Ψ_3 should result in a decrease in the stabilization afforded to the system. In addition, there is more π-space electron repulsion in the five-electron systems relative to the three-electron systems.

Pentadienyl-Type Delocalized Radicals. Pentadienyl Radical (48). The pentadienyl radical has been generated by hydrogen atom abstraction from 1,2-pentadiene[46] and the ring opening of the 2-cyclobutenylmethyl radical[47] and has been studied by ESR techniques. Two stereoisomers of **48** have been detected, the W- and Z-conformations **48a** and **48b**. The stabilization energy of **48** has been estimated to be approximately 25 kcal/mol based on the energy barrier for the isomerization of **48b** to **48a**.[46] Thermochemical estimates suggest a value of approximately 18.5 kcal/mol based on the bond dissociation energy of a secondary C–H bond.[48] Studies on the thermodynamics of the dissociation of a methyl group in 1,3-hexadiene[49] and 3-methyl-1,4-pentadiene[50] indicate the resonance energy of the pentadienyl radical to be 18.6 and 18.5 kcal/mol, respectively.

The results of several theoretical studies on **48** have been reported. Unfortunately, complete geometry optimization has not
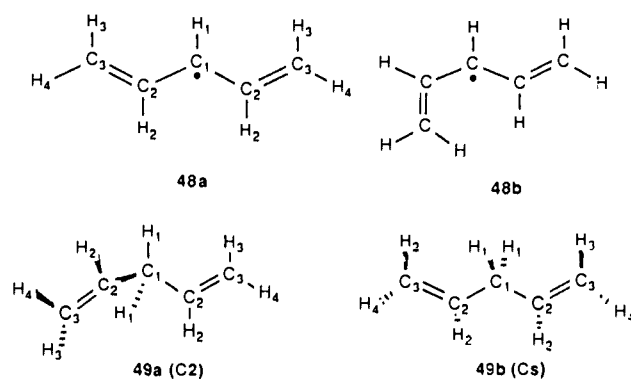
been carried out, or if it has been, the geometrical parameters have not been reported.[51] In the present study calculations have been carried out only on the lowest energy conformation **48a**.[55] Two minimum-energy conformations have been located for 1,4-pentadiene, **49a** and **49b**, with the former lower in energy by 0.71 kcal/mol. The kinetic RSE relating **48a** with **49b** is +20.32 kcal/mol, in good agreement with the experimentally based estimates. The kinetic ΔRSE relating **48a** with **49b** is +4.72 kcal/mol, while the thermodynamic ΔRSE relating **48a** with **49a** is +4.01 kcal/mol. Both of these ΔRSE's indicate the presence of considerable extra stabilization in the pentadienyl radical relative to twice that of the allyl radical.

Cyanovinylmethyl Radical (50). Calculations have been previously carried out on the E and Z conformations **50a** and **50b**
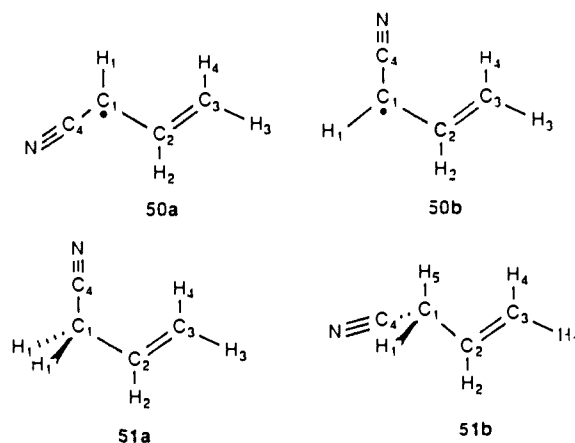
at the UHF 4-31G level, giving total energies of −207.90840 and −207.90764 au with RSE's of +17.19 and +16.69 kcal/mol, respectively.[26b] The present calculations at the ROHF 4-31G level

(46) MacInnes, I.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1073.

(47) Davies, A. G.; Griller, D.; Ingold, K. U.; Lindsay, D. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 633.

(48) McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. Egger, K. W.; Jola, M. *Int. J. Chem. Kinet.* **1970**, *2*, 265.

(49) Trenwith, A. B. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3131.

(50) Trenwith, A. B. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 266.

(51) Calculations have been carried out at the ab initio level using a minimal STO basis expanded as a sum of two GTOs with all C–C and C–H bond lengths fixed at 1.40 and 1.09 Å, respectively, and with all bond angles assigned values of 120°.[52] Similar calculations have been carried out by using a Dunning (10s,6p) basis set contracted to [5s,4p]; but no indication of the geometrical parameters was given.[52b] Calculations at the UHF INDO level have been carried out on the conformations of **48** with apparent optimization of the C–C bond lengths.[50] C–C bond lengths of 1.38 Å were reported for the W- and Z-conformations of **48**, and 1.42 Å for the U-conformation.[53] Calculations have also been carried out at the UHF MINDO/3 level[54] and UHF MNDO level;[46] however, no geometrical parameters were reported. The results of all of the calculations indicated that the W-conformation was lowest in energy.

(52) Hinchliffe, A.; Cobb, J. C. *J. Mol. Struct.* **1974**, *23*, 273. Hinchliffe, A. *Ibid.* **1975**, *27*, 329.

(53) Sustmann, R.; Schmidt, H. *Chem. Ber.* **1979**, *122*, 1440.

(54) Bews, J. R.; Glidewell, C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1447.

(55) The results of the present calculations indicate a structure for the pentadienyl radical with extensive bond localization; the C_1–C_2 bond length is calculated to be 1.332 Å and the C_2–C_3 bond length 1.431 Å. Full geometry optimization calculations at the UHF 4-31G level also indicate bond localization with C_1–C_2 and C_2–C_3 bond lengths of 1.373 and 1.411 Å, respectively. The concern is whether the calculations have found a true minimum-energy structure or have settled on a false minimum corresponding to the most important resonance contributing structure. An analysis of the occupied wave functions indicates that a bond-localized structure is to be expected.

give energies for **50a** and **50b** of -207.87994 and -207.87984 au, respectively. Two minimum-energy conformations have been located for 3-cyano-1-propene, **51a** and **51b**, with the former being lower in energy by 0.07 kcal/mol. The kinetic RSE's relating **50b** with **51a** and **50a** with **51b** are +15.81 and +15.94 kcal/mol, in reasonable agreement with the UHF-based results. The ΔRSE's are +2.67 and +2.80 kcal/mol, respectively, indicating the presence of extra stabilization in these radicals relative to the sum of the RSE's of the singly substituted radicals.
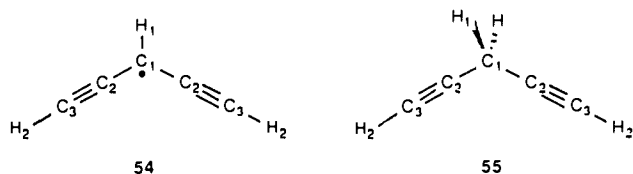
Formylvinylmethyl Radical (52). Calculations indicate that the formylvinylmethyl radical exists in the four conformations **52a–d**,
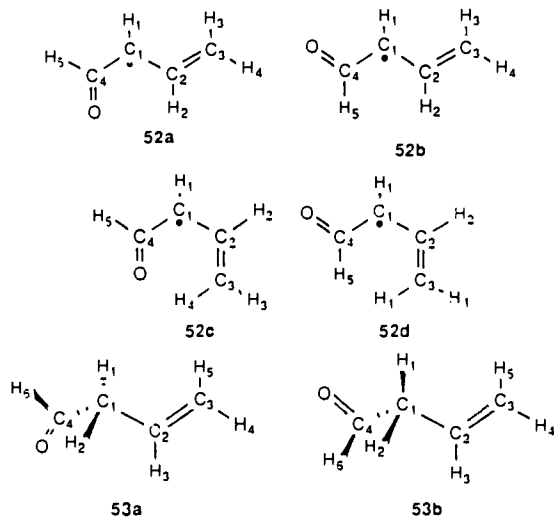

with **52a** being lowest in energy followed by **52b** (+0.57 kcal/mol), **52c** (+1.68 kcal/mol), and **52d** (+2.91 kcal/mol). Only two conformations have been located for 3-butenal (**53a** and **53b**), in which the C_1–H_1 bond is essentially eclipsed with the C=O bond. Conformations having the formyl group eclipsed with the C=C bond do not appear to represent local minimum-energy structures. The kinetic and thermodynamic ΔRSE relating **52a** with **53a** is +3.55 kcal/mol, while the kinetic ΔRSE relating **52b** with **53b** is +3.22 kcal/mol. Both values indicate the presence of considerable extra stabilization.

In this series of substituted vinylmethyl radicals, all are indicated to possess extra stabilization over the sum of the stabilizations present in the singly substituted radicals. One may ask how does the captodative concept apply to this series of disubstituted radicals? The answer to this question depends on how one characterizes the acceptor–donor properties of the vinyl group. It is obvious that in the presence of stronger electron-withdrawing groups the vinyl group can act as an electron donor, in which case these results would be consistent with the captodative concept.

Diethynylmethyl Radical (54). The RSE and ΔRSE for the diethynylmethyl radical are +16.70 and +0.70 kcal/mol, respectively. The value of the ΔRSE indicates that **54** possesses a very slight extra stabilization.

Cyanoethynylmethyl Radical (56). The RSE calculated for **56** is +14.30 kcal/mol, with a ΔRSE of +0.96 kcal/mol indicating the presence of a slight extra stabilization.
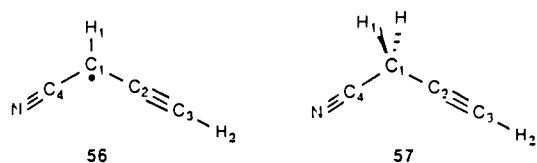

Ethynylformylmethyl Radical (58). The ethynylformylmethyl radical can exist in either of the two conformations **58a** or **58b**,
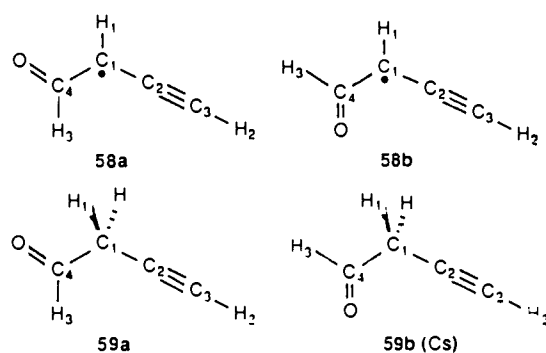
with the former being lower in energy by 1.71 kcal/mol. Only two minimum-energy conformations could be located for 3-butynal, **59a** and **59b**, with the former being lower in energy by 1.51 kcal/mol. The kinetic and thermodynamic RSE and ΔRSE relating **58a** with **59a** are +16.13 and +0.47 kcal/mol. The RSE and ΔRSE relating **58b** with **59b** are +15.93 and +0.27 kcal/mol. These ΔRSE values indicate the presence of a slight extra stabilization in these radicals.

In this series of substituted ethynylmethyl radicals, the calculations indicate that all possess some extra stabilization, but to a lesser degree than in the substituted vinylmethyl radicals. This would appear to be due to the slightly greater electronegativity of the ethynyl group relative to the vinyl group.

Dicyanomethyl Radical (60). The calculated RSE for **60** is +11.17 kcal/mol, with a ΔRSE of +0.49 kcal/mol indicating the presence of a slight extra stabilization in **60**. This result is not
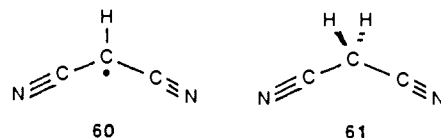

in accord with the captodative concept, which predicts that this dicaptor-substituted radical will suffer net destabilization relative to twice the RSE of the cyanomethyl radical.

Cyanoformylmethyl Radical (62). Calculations indicate that there are two minimum-energy conformations for the cyanoformylmethyl radical, **62a** and **62b**, with the former being lower
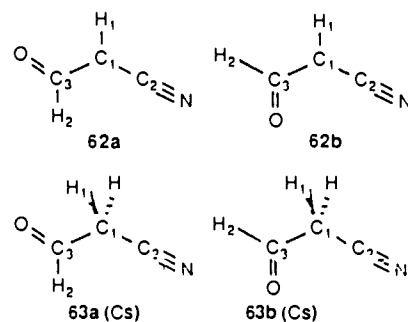
in energy by 1.34 kcal/mol. Two conformations have been located as local minima for cyanoacetaldehyde, **63a** and **63b**, with the former being lower in energy. The kinetic and thermodynamic RSE and ΔRSE relating **62a** with **63a** are +12.35 and -0.65 kcal/mol. The kinetic RSE and ΔRSE relating **62b** with **63b** are +12.04 and -0.95 kcal/mol. This dicaptor-substituted radical is slightly destabilized relative to the sum of the RSE's of the singly substituted radicals.

Diformylmethyl Radical (64). Calculations have been carried out on only the expected lowest energy conformation of **64**. The energy surface of propanedial (diformylmethane) appears to be very complex and relatively flat. One conformational minimum (**65**) has been located which is kinetically related to **64**. In **65** the formyl groups do not prefer to be eclipsed with either of the methylene C–H bonds. The RSE and ΔRSE for **64** are +14.73

64   65 (Cs)
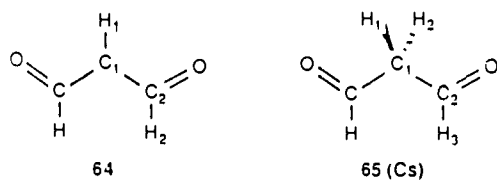
and −0.59 kcal/mol. The value of the ΔRSE indicates the presence of slight destabilization in **64** relative to twice the RSE for the formylmethyl radical.

In this final series of cyano- and formyl-substituted methyl radicals there is no indication of a significant destabilization being present in the dicaptor-substituted radicals, even in the very highly electronegatively substituted diformylmethyl radical.

Summary of the Pentadienyl-Type Delocalized Radicals. The calculated ΔRSE's of the pentadienyl-type, five-electron delocalized radicals mostly indicate that these systems possess slight extra stabilization relative to the sum of the stabilizations present in the singly substituted methyl radicals, even in systems containing two relatively strong electron-withdrawing functions. This is not consistent with the captodative concept, which would have predicted net destabilization in such systems.

A simple MO analysis provides some insight as to why this is so. In the pentadienyl-type systems, the bonding MO's Ψ_1 and Ψ_2 are doubly occupied, with the SOMO being the nonbonding pentadienyl MO Ψ_3. In this case it is not necessary to occupy an antibonding MO as in the case of the butadiene-type, five-electron radicals. A further stabilization is gained by the decreased π-space electron repulsion in the pentadienyl-type systems compared to the butadiene-type systems.

Summary

The results of the present calculations indicate that substantial captodative stabilization is present only in the allyl-type, three-electron radicals **9, 11,** and **13**. The results of the calculations on the butadiene-type, five-electron, donor–acceptor substituted radicals **36, 38,** and **42** predict weak net *destabilization*, while the results on **40, 44,** and **46** predict weak net *stabilization. There is no evidence for the existence of a significant captodative stabilization in these donor–acceptor substituted radicals.* The stabilization and destabilization effects are very sensitive to the relative electronegativity of the substituents attached to the radical centers. The calculations on the pentadienyl-type, five-electron

radicals indicate the presence of slight to moderate extra stabilization not anticipated by the captodative concept, except for the highly electronegatively substituted radicals **62** and **64**. The trends in the ΔRSE's have been discussed in terms of the type of MO's and their occupancy and the relative electronegativity of the attached substituents.

The present results suggest that the results of many studies that have been interpreted in terms of supporting the captodative concept may need to be reevaluated, in particular those reactions that involve radical formation by radical additions to substituted alkenes and allenes. In such radical addition reactions the transition states are expected to occur early along the reaction coordinates in which reactant ground state electronic properties are expected to control reactivity, and not substituent effects on the developing radical center.

In the isomerization reactions of the substituted allyl radicals discussed in the introduction, the present calculations indicate that the observed trend in energy barriers cannot be explained on the basis of a captodative stabilization in the transition state for the isomerization of the 1-cyano-1-methoxyallyl radical. In this isomerization reaction ground state destabilization must be the major contributing factor causing the lowering of the energy barrier for isomerization. Further theoretical studies will be devoted to analyzing these effects.

In view of the general conclusions arrived at in this article, it is instructive to inquire as to why the approach to the captodative effect based on resonance theory is not universally valid. This would appear to be due to the fact that it was only the *number* of resonance contributing structures that was considered in the analysis of the substituted radicals, and not their relative importance. If all of the resonance structures considered contributed equally to the resonance hybrid, then the analysis would have been correct. In fact, consideration of the charge separations in some of the contributing structures to **3** would indicate that some structures would contribute to a much smaller extent, thus flawing the approach.

Influencing Reactivity by Monolayer Compression: An Alcohol Dehydration

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Abstract: The kinetics of the acid-catalyzed dehydration of 1,1-diphenyl-1-octadecanol have been examined at the air–liquid interface. The rate of reaction was found to be strongly dependent on the area/molecule in the monolayer. For expanded films with large areas/molecule the rate of dehydration was over 20 times that for compressed films. The results have been interpreted in terms of the availability of the β-hydrogens to the acid subphase. With highly expanded films the hydrophobic chains are deduced to be essentially independent, affording facile access of the subphase to the β-hydrogen. For compressed films and those of intermediate areas/molecule the hydrophobic chains are interacting and the β-hydrogens are oriented away from the subphase. A threshold value of the area/molecule for β-hydrogen access has been determined.

Reactions in monolayer assemblies provide the opportunity to examine the reactivity of molecules constrained in a plane. The geometrical requirements of transition states may be inferred from

the reactivity of the films at varying areas/molecule allowed to the monolayer; e.g., the acid-catalyzed cyclization of the monoterpenoid alcohol nerol is strongly disfavored at low areas/mol-