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Substituent Effects. 6. Heterosubstituted Allyl Radicals. Comparison with Substituted Allyl Cations and Anions

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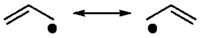
Abstract: The energies, bond orders, and spin polarizations of a series of $CH_2{=}CH{-}XH_n^{\bullet}$ radicals were calculated at the UMP2/6-311+G**, Becke3LYP/6-311+G**, and QCISD/6-311G** theoretical levels, and the energies also were obtained at the G2(MP2) theoretical level. The energies of the parent compounds were obtained in the same fashion and their bond dissociation energies were derived from these data. The Becke3LYP and the G2(MP2) energies predicted essentially the same stabilization energies for the radicals, and stabilization was found mainly with allyl itself and with the vinyl thiol radical indicating that stabilization requires that the terminal atoms have similar electronegativities. A study of related radicals also indicated that stabilization is lost when the central atom has a different electronegativity. Therefore, stabilization of the allyl radical appears to require that all three atoms in the allyl system have similar electronegativities. It is found that the radical center prefers to be at the less electronegative atom. When the terminal atoms have similar electronegativities, the odd electron is shared between them, and the center atom becomes spin polarized in the opposite sense. Spin polarizations calculated from Becke3LYP and QCISD wave functions are essentially the same, but those calculated from MP2 wave functions are often incorrect as a result of spin contamination. The results obtained with the allyl radicals are compared with corresponding data for allyl cations and anions.

1. Introduction

We have examined the effects of substituents on neutral molecules,[1] carbocations,[2] and carbanions.[3] These compounds have an advantage, as far as interpretation is concerned, of being closed shell species. Free radicals, having an unpaired electron, present the possibility for another type of interaction, associated with spin polarization.[4] Partially separating the α and β spin electrons might provide a means for reducing electron repulsion, and thus increasing stability. The allyl radicals provide an example of spin polarization that has been examined both experimentally[5,6] and theoretically.[7,8]

The allyl radical has been assigned a 15 kcal/mol resonance stabilization based on the measured barrier to rotation[9] and this is in agreement with the difference in C−H bond dissociation energies for propene and propane (14 kcal/mol).[10,11] However, if one considers the resonance structures written for the allyl radical



in either one there is a p orbital with one electron at each carbon. It is not obvious why the average structure should have an energy much lower than either of the resonance structures. It may be that part of the observed stabilization is derived from spin polarization.

In order to gain further information on both spin polarization and resonance stabilization in this conjugated system, we have examined the replacement of the terminal CH_2 group in an allyl radical with a variety of other groups including Be, BH, NH, O, Mg, AlH, SiH_2, PH, and S. There have, of course, been previous studies of allyl radicals.[12] Davidson, Feller, and Borden[13] have examined the question of when allylic resonance is important, and their conclusion that resonance stabilization is decreased when the electronegativities of the terminal atoms increase has been confirmed experimentally by Bordwell, Ji, and Zhang.[14] Coolidge, Hrovat, and Borden have studied the vinylsilyl radical and found that the odd electron prefers to be at the silicon.[15] This agrees with experimental studies.[16]

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Nicolaides and Borden have studied the 1,1-difluoroallyl radical[17] and showed that the rotational barriers are affected by the pyramidalization of the CF_2 group when it rotates and by the strengthening of the $CF_2{=}CH$ π bond when the CH_2 group rotates. Glaser and Choy have studied the effect of spin contamination on electron and spin densities in allyl radicals.[8] They found that whereas spin contamination had only a small effect on the total electron populations, it did have an important effect on the spin populations. The previous studies have not examined as wide a range of substituents as in this report, and the calculations were carried out at lower theoretical levels than are now practical.

2. Calculations

All ab initio calculations were carried out using GAUSSIAN-93.[18] The structures were obtained by geometry optimization at the MP2/6-31G* level, and zero-point energies were estimated at the HF/6-31G* level, scaling the calculated frequencies by 0.893.[19] The radicals were studied at the corresponding UMP2 and UHF levels. Many of the radicals had extensive spin contamination ($s^2 \sim 0.9-1.0$), and therefore single point QCISD calculations[20] were performed using the UMP2 geometries. It is known that QCISD is quite effective in removing spin contamination.[21] Density functional theory (DFT) also appears to be less susceptible to spin contamination than are UHF and UMP2,[22] and DFT calculations were carried out for both the precursors and the corresponding radicals. The DFT results were obtained using the three-parameter Becke3LYP functional[23] which is a hybrid of exact (Hartree–Fock) exchange terms and gradient-corrected exchange and correlation terms, similar to that first suggested by Becke.[24] Numerical integrations were carried out using Becke's scheme[25] and grids consisting of 100 radial points and 302 angular points for each atom were used for all calculations. The calculations were carried out with both the 6-311G** and 6-311+G** basis sets using the MP2/6-31G* optimized geometries in order to see if diffuse functions might be important in describing the radicals. There was little difference in the energy changes calculated using the two sets, and only the energies derived from the latter are given in the Table. Similarly, there was essentially no difference in the properties derived from the two sets of wave functions via integration of charge density.[26] It was also of special interest to be able to compare the results obtained using DFT with those found with QCISD in order to see how effective DFT is in minimizing spin contamination in allyl radicals that are highly contaminated at the RHF and MP2 levels of theory. In the case of the allyl radical itself, Sim et al. have found DFT to give satisfactory spin densities.[27]

Since bond dissociation energies provide one of the more important tools for studying the stability of radicals, we have also made use of the recently developed G2(MP2) model.[28] It has been found to be remarkably effective in reproducing bond dissociation energies, giving results comparable to Pople's G2 model,[19] but with considerably less computational effort. It is effectively QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* plus the zero-point energy and a higher level correction.

The analysis of the wave functions using Bader's theory of atoms in molecules (AIM)[29] was carried out using PROAIMV.[30] The bond orders were obtained from the atomic overlap matrices by the procedure of Cioslowski and Mixon,[31] making use of BONDER. The charge density difference plots were prepared using the CASGEN series of programs developed at Yale.[32]

3. Vinyl–X• Radicals

Geometry optimizations for all of the compounds in this report were carried out at the MP2/6-31G* theoretical level that is known to normally give structural data that are in good accord with experimental observations.[33,34] The MP2/6-311+G*, Becke3LYP/6-311+G**, and G2(MP2) energies were obtained using these geometries and are given in Table 1. Here, it should be noted that the G2(MP2) energies include the zero-point energies. The structural data of principal interest are the C=C and C–X bond lengths (Table 2). The lengths are those obtained in the MP2/6-31G* geometry optimizations, and the bond orders were calculated via the procedure developed by Cioslowski and Mixon.[31] Both the MP2/6-31G* and QCISD/6-311G** wave functions were used in these calculations. the C=C bond lengths were found to be related to the bond orders (Figure 1), and the two sets of bond orders, although somewhat different numerically, are linearly related (Figure 2). The bond orders obtained at the two theoretical levels would be expected to be somewhat different because the degree of correction for electron correlation will change the charge distribution in bonds.[35] The good correlation between the two sets of bond orders again suggests that the spin contamination in the radicals does not lead to important changes in the total charge density distribution.[8]

The question of the stabilization of the radicals is of considerable interest.[13] One way to obtain information related to this question is via an examination of the X–H bond dissociation energies. However, there is a considerable variation

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Table 1. Calculated Energies (hartrees)

compd	MP2/6-31G*	ZPE[a]	MP2/6-311+G**	B3LYP/6-311+G**	G2(MP2)
$CH_2=CH-BeH$	−92.957 23	29.5	−93.061 94	−93.355 86	−93.094 57
$CH_2=CH-BH_2$	−103.626 23	37.5	−103.741 97	−104.060 35	−103.781 25
$CH_2=CH-CH_3$	−117.469 66	47.9	−117.602 69	−117.945 51	−117.642 56
$CH_2=CH-NH_2$	−133.491 28	41.6	−133.635 79	−133.994 75	−133.688 20
$CH_3-CH=NH$	−133.503 76	41.4	−133.642 68	−133.998 34	−133.694 59
$CH_2=CH-OH$	−153.332 16	34.2	−153.486 75	−153.865 42	−153.555 21
$CH_3-CH=O$	−153.358 97	33.6	−153.505 82	−153.881 72	−153.572 96
$CH_2=CH-MgH$	−277.895 42	27.3	−278.120 93	−278.686 27	−278.045 51
$CH_2=CH-AlH_2$	−320.828 48	32.8	−321.064 24	−321.658 59	−321.002 17
$CH_2=CH-SiH_3$	−368.463 11	40.2	−368.713 22	−369.337 09	−368.661 87
$CH_2=CH-PH_2$	−419.701 92	36.3	−419.947 13	−420.587 82	−419.912 45
$CH_2=CH-SH$	−475.935 93	31.0	−476.172 22	−476.833 32	−476.154 15
$CH_2=CH-Be^\bullet$	−92.319 80	24.7	−92.416 85	−92.698 05	−92.445 48
$CH_2=CH-BH^\bullet$	−102.962 30	30.7	−103.072 19	−103.381 90	−103.111 91
$CH_2=CH-CH_2^\bullet$	−116.824 29	38.9	−116.948 87	−117.298 11	−117.003 06
$CH_2=CH-CH_2^\bullet$, rot TS	−116.805 06	38.1	−116.930 24	−117.270 00	−116.978 72
$CH_2=CH-NH^\bullet$	−132.846 96	32.8	−132.976 31	−133.342 91	−133.046 54
$CH_2=CH-O^\bullet$	−152.698 44	25.3	−152.837 53	−153.221 00	−152.920 13
$CH_2=CH-Mg^\bullet$	−277.299 02	23.8	−277.515 58	−278.068 86	−277.433 17
$CH_2=CH-AlH^\bullet$	−320.205 52	28.1	−320.431 78	−321.016 81	−320.365 66
$CH_2=CH-SiH_2^\bullet$	−367.825 11	33.9	−368.065 14	−368.685 69	−368.017 29
$CH_2=CH-PH^\bullet$	−419.085 79	29.6	−419.318 02	−419.960 87	−419.290 78
$CH_2=CH-S^\bullet$	−475.315 88	24.8	−475.535 81	−476.201 27	−475.527 07
CH_3BeH	−54.992 86	25.3	−55.072 56	−55.271 17	−55.086 84
CH_3BH_2	−65.655 64	33.2	−65.745 01	−65.968 06	−65.766 56
CH_3CH_3	−79.503 97	44.7	−79.609 27	−79.856 50	−79.628 93
CH_3NH_2	−95.514 44	38.6	−95.631 61	−95.893 66	−95.664 51
CH_3OH	−115.353 29	31.0	−115.482 66	−115.764 81	−115.531 81
CH_3MgH	−239.930 83	23.3	−240.130 80	−240.601 68	−240.036 72
CH_3AlH_2	−282.861 49	28.5	−283.071 48	−283.571 36	−282.991 56
CH_3SiH_3	−330.500 39	36.5	−330.724 02	−331.253 58	−330.653 50
CH_3PH_2	−381.736 89	32.9	−381.954 44	−382.501 53	−381.900 67
CH_3SH	−437.967 88	27.8	−437.176 24	−438.743 04	−438.141 23
$CH_3Be^\bullet$	−54.358 24	20.8	−54.429 76	−54.614 70	−54.438 65
$CH_3BH^\bullet$	−64.996 73	26.4	−65.079 59	−65.293 21	−65.100 76
$CH_3CH_2^\bullet$	−78.844 66	35.5	−78.942 04	−79.184 92	−78.968 11
$CH_3NH^\bullet$	−94.860 87	29.6	−94.963 86	−95.225 59	−95.005 95
$CH_3O^\bullet$	−114.693 09	22.6	−114.804 41	−115.091 89	−114.863 45
$CH_3Mg^\bullet$	−239.336 68	20.0	−239.527 25	−239.985 79	−239.425 07
$CH_3AlH^\bullet$	−282.241 08	24.0	−282.441 00	−282.931 10	−282.356 12
$CH_3SiH_2^\bullet$	−329.866 38	30.8	−330.078 91	−330.599 90	−330.006 51
$CH_3PH^\bullet$	−381.122 37	26.6	−381.327 14	−381.866 21	−381.272 03
$CH_3S^\bullet$	−437.345 98	21.6	−437.538 72	−438.100 28	−437.503 04

[a] HF/6-31G* scaled by 0.893 kcal/mol.

Table 2. Structural Properties of $CH_2=CHX$ Radicals, MP2/6-31G*

	radical				parent	
	C=C		C−X		C=C	C−X
X	length	bond order	length	bond order	length	length
Be	1.320	2.068	1.680	0.347	1.351	1.670
BH	1.315	2.020	1.540	0.615	1.351	1.539
CH_2	1.378	1.452	1.378	1.452	1.336	1.498
NH	1.402	1.236	1.297	1.409	1.340	1.400
O	1.456	1.060	1.200	1.361	1.336	1.367
Mg	1.324	2.046	2.094	0.368	1.351	2.084
AlH	1.322	2.023	1.953	0.458	1.350	1.942
SiH_2	1.310	2.031	1.872	0.567	1.343	1.865
PH	1.331	1.875	1.786	0.930	1.339	1.833
S	1.346	1.715	1.702	1.306	1.337	1.759

QCISD/6-311G** Bond Orders

	C=C	C−X		C=C	C−X
Be	1.874	0.354	Mg	1.875	0.355
BH	1.808	0.614	AlH	1.855	0.436
CH_2	1.399	1.399	SiH_2	1.838	0.560
NH	1.225	1.353	PH	1.753	0.904
O	1.086	1.304	S	1.625	1.285

in these energies even when there is no possibility of a π-interaction. In order to correct for this, we have examined the reactions shown in Table 3, for which the intrinsic changes in X−H BDE's will cancel. It is interesting to note that the B3LYP transfer energies are quite close to those obtained using G2(MP2) whereas the MP2/6-311+G** transfer energies are sometimes significantly different. It might also be noted that the bond dissociation energies calculated at the G2(MP2) and B3LYP levels are generally quite close to each other (Table 4), and when they differ (as with the oxygen-containing radicals), the deviation is about the same for the oxyallyl and methoxy radicals.

One measure of the similarity between the B3LYP and QCISD wave functions can be obtained by comparing differences in atomic populations (AIM) obtained from these two wave functions. In general, a change in total atomic population arises from charge reorganization within the atomic basins and also from shifts in the interatomic surfaces defining the atomic basin. In order to more directly compare charge distributions obtained from different levels of theory, it is useful to examine both the changes in atomic populations arising from charge reorganization within the basis (Δ*n*(basin)) and also the changes due to shifts in the interatomic surfaces (Δ*n*(surface)). These differences obtained by comparing the B3LYP and QCISD wave functions are given in Table 5 for vinylberyllium and allyl and vinyloxy radicals and can be seen to be quite small. The group

Table 3. Calculated Hydrogen Atom Transfer Energies, 6-311+G**

reaction	ΔH, 0 K, kcal/mol MP2	B3LYP	G2(MP2)
$CH_2{=}CH{-}BeH + CH_3Be^{\bullet} \rightarrow CH_2{=}CH{-}Be^{\bullet} + CH_3BeH$	+1.1	+0.5	+0.6
$CH_2{=}CH{-}BH_2 + CH_3BH^{\bullet} \rightarrow CH_2{=}CH{-}BH^{\bullet} + CH_3BH_2$	+2.7	+2.3	+2.2
$CH_2{=}CH{-}CH_3 + CH_3CH_2^{\bullet} \rightarrow CH_2{=}CH{-}CH_2^{\bullet} + CH_3CH_3$	−8.2	−15.0	−13.4
$CH_2{=}CH{-}NH_2 + CH_3NH^{\bullet} \rightarrow CH_2{=}CH{-}NH^{\bullet} + CH_3NH_2$	−5.0	−10.0	−10.6
$CH_3{-}CH{=}NH + CH_3CH_2^{\bullet} \rightarrow CH_2{=}CH{-}NH^{\bullet} + CH_3CH_3$	+0.1	−9.5	−8.0
$CH_2{=}CH{-}OH + CH_3O^{\bullet} \rightarrow CH_2{-}CH{=}O + CH_3OH$	−18.7	−18.4	−20.9
$CH_3{-}CH{=}O + CH_3CH_2^{\bullet} \rightarrow CH_2{-}CH{=}O + CH_3CH_3$	+1.6	−5.9	−5.0
$CH_2{=}CH{-}MgH + CH_3Mg^{\bullet} \rightarrow CH_2{=}CH{-}Mg^{\bullet} + CH_3MgH$	+0.9	+0.8	+0.4
$CH_2{=}CH{-}AlH_2 + CH_3AlH^{\bullet} \rightarrow CH_2{=}CH{-}AlH^{\bullet} + CH_3AlH_2$	+1.0	+0.8	+0.7
$CH_2{=}CH{-}SiH_3 + CH_3SiH_2^{\bullet} \rightarrow CH_2{=}CH{-}SiH_2^{\bullet} + CH_3SiH_3$	+1.3	−2.2	−1.5
$CH_2{=}CH{-}PH_2 + CH_3PH^{\bullet} \rightarrow CH_2{=}CH{-}PH^{\bullet} + CH_3PH_2$	+0.7	−5.6	−4.4
$CH_2{=}CH{-}SH + CH_3S^{\bullet} \rightarrow CH_2{=}CH{-}S^{\bullet} + CH_3SH$	−0.7	−6.7	−7.0

Table 4. Calculated X−H Bond Dissociation Energies, kcal/mol, 0 K[a]

compd	BDE MP2	B3LYP	G2(MP2)	compd	BDE MP2	B3LYP	G2(MP2)
$CH_2{=}CHBeH$	86.4	94.3	93.6	CH_3BeH	85.2	93.8	93.0
$CH_2{=}CHBH_2$	99.9	105.3	106.3	CH_3BH_2	97.1	103.0	104.0
$CH_2{=}CHCH_3$	87.6	83.6	87.5	CH_3CH_3	95.9	98.6	100.9
$CH_2{=}CHNH_2$	91.4	86.6	88.9	CH_3NH_2	96.4	96.6	99.5
$CH_2{=}CHOH$	84.9	81.8	84.8	CH_3OH	103.6	100.2	105.6
$CH_2{=}CHMgH$	62.7	70.3	70.5	CH_3MgH	61.8	69.5	70.1
$CH_2{=}CHAlH_2$	78.5	84.4	85.7	CH_3AlH_2	77.5	83.6	85.0
$CH_2{=}CHSiH_3$	86.7	88.7	90.7	CH_3SiH_3	85.5	90.9	92.2
$CH_2{=}CHPH_2$	74.4	73.1	76.3	CH_3PH_2	73.7	78.7	80.7
$CH_2{=}CHSH$	79.5	76.8	79.7	CH_3SH	80.2	83.5	86.7

[a] The MP2 and B3LYP calculations made use of the 6-311+G** basis set.

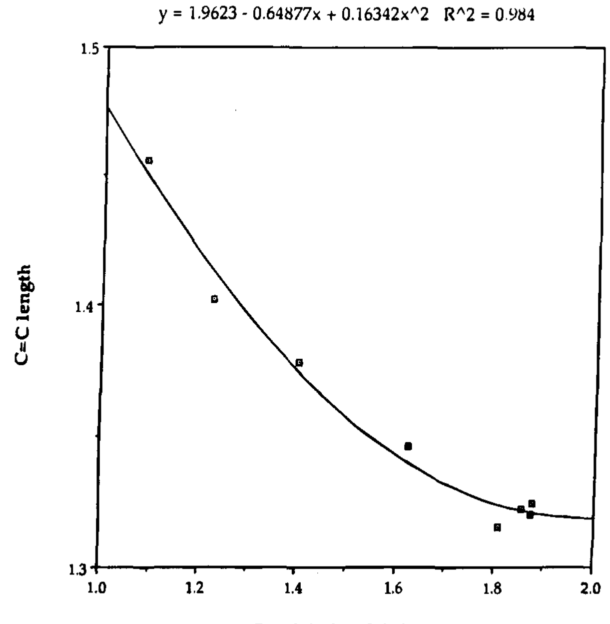

Figure 1. Correlation between the C═C bond lengths and the covalent bond orders calculated from the QCISD wave functions.

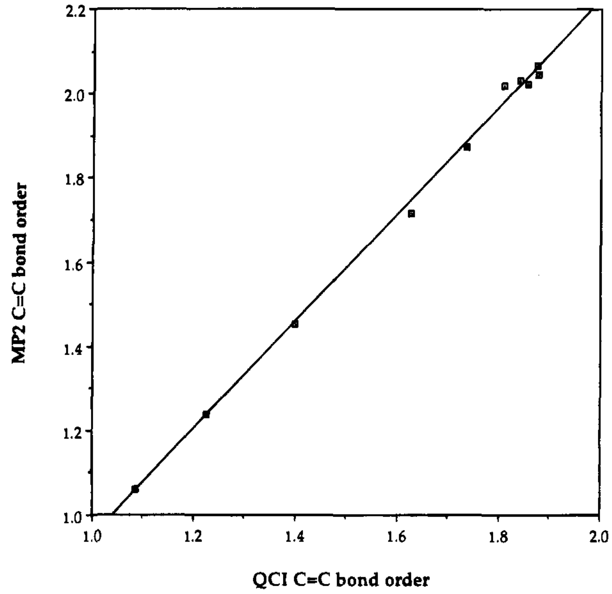

Figure 2. Correlation between the C═C covalent bond orders derived from MP2 and QCISD wave functions.

charges derived from the Mulliken population analysis and integration of the charge density (AIM) are summarized in Table 6. As is often the case, the two sets of populations differ considerably. The reasons for the differences have been discussed.[26]

With propene, the hydrogen atom transfer is exothermic by 13 kcal/mol, and this is commonly taken as the resonance stabilization of the allyl radical. The value is in agreement with the calculated (Table 1) and observed[9] rotational barrier (15 kcal/mol) which provides another estimate of the resonance stabilization.[11] Vinyl alcohol gives an even more exothermic reaction. Does this mean that the vinyloxy radical has greater stabilization than allyl? This is probably not the case, as suggested by the bond lengths and bond orders.

The C═C bond lengths of the radicals increase on going from Be to O as the substituent, and the bond orders correspondingly decrease. Thus with Be or BH as the substituent, the C═C bond is essentially intact and the radical must reside mainly on the heteroatom. With O as the substituent, the C−C bond is essentially a single bond, and the C−O bond has reached a length corresponding to a C═O. Thus, the odd electron is largely at the terminal C instead of the oxygen.[36] The C═O

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[36] This conclusion also has been reached based on experimental EPR studies of 2-alkanoyl radicals: ref 6.

Table 5. Charge Shifts on Going from DFT to QCISD Wave Functions[a]

atom[b]	Δn(basin)	Δn(surface)	Δn(total)
	a. CH_2=CH–Be		
Be	−0.003	−0.010	−0.013
C	−0.007	−0.001	−0.008
H	0.007	0.001	0.008
C	−0.010	0.004	−0.006
H	0.006	0.002	0.009
H	0.006	0.003	0.010
	b. CH_2=CH–CH_2•		
C	−0.013	−0.002	−0.015
H	0.006	0.001	0.006
H	0.006	0.001	0.007
C	−0.005	−0.001	−0.006
H	0.007	0.001	0.008
	c. CH_2=CH–O•		
O	−0.004	0.027	0.023
C	−0.019	−0.032	−0.051
H	0.006	0.004	0.010
C	0.000	−0.001	0.000
H	0.007	0.002	0.009
H	0.008	0.002	0.010

[a] $\Delta n(\text{total}) = n^{\text{QCISD}}_{\text{QCISD}} - n^{\text{B3LYP}}_{\text{B3LYP}}$, $\Delta n(\text{basin}) = n^{\text{QCISD}}_{\text{B3LYP}} - n^{\text{B3LYP}}_{\text{B3LYP}}$, $\Delta n(\text{surface}) = \Delta n(\text{total}) - \Delta n(\text{basin})$, where the superscript denotes the wave function used for the integration and the subscript denotes the wave function used to define the atomic basin. [b] The atoms are listed from right to left, and the attached hydrogens are given directly below the specified atom.

covalent bond order is not 2 because it has a· large polar contribution (cf. the group charges in Table 6). The bond order is typical of C=O bonds.[31b] It is well-known that C=O bonds are considerably stronger than C=C bonds,[37] and the effective conversion of a C=C bond to a C=O bond in forming the radical from vinyl alcohol must be a significant factor in leading to the more exothermic reaction of vinyl alcohol. In view of the structure of the radical, a better estimate of its stabilization would be obtained by examining the abstraction of a methyl hydrogen from acetaldehyde by an ethyl radical (Table 3). Now, the reaction center is a carbon on both sides of the reaction and it is exothermic by only 5 kcal/mol. Vinylamine is an intermediate case. Here, abstraction of an NH hydrogen of vinylamine by $CH_3NH^•$ is only slightly more exothermic than abstraction of a CH hydrogen of 1-azapropene by $C_2H_5^•$.

With the second-row substituents, it is only with S that there is a significant change in the C=C bond length or bond order upon hydrogen abstraction. The structural data suggest that the other substituents place most of the odd spin on the heteroatom in the radicals. Similarly, the largest stabilization energy for second-row substituents is found with the radical derived from vinyl thiol. It appears that the stabilization of the allyl-type radicals is favored by having terminal atoms with similar electronegativities.

These structural conclusions regarding the preferred site for the odd electron can be checked by examining the spin polarization (Table 7). The UMP2/6-31G* values are unusual, and appear to be skewed by the spin contamination. Thus, when X = Be, BH_2, Mg, and AlH, the MP2 wave functions suggest extensive spin polarization that is not in accord with the other compounds in the series or with the spin polarization found using other wave functions. It is known that spin populations are more sensitive to spin contamination than is the total charge density,[8] and so it is not surprising to find problems with the UMP2 spin populations.

The QCISD spin polarizations are closer to one's expectations, and fit in well with the conclusions from the structural study. In addition, the B3LYP wave functions lead to spin polarizations that are close to those found with QCISD. Thus, with Be or BH as the substituent, essentially all of the α spin is found on the heteroatom. With allyl itself, the two terminal carbons bear equal α populations, but there is considerable excess *β* population at the central carbon. On going to NH and O as the substituent, the α spin density shifts toward the terminal carbon and the amount of excess *β* spin density at the central carbon decreases.

The second-row substituents show a similar pattern, with most

Table 6. Net Group Charges[a]

	Mulliken/QCISD			AIM/B3LYP			AIM/QCISD		
compd	CH_2	CH	X	CH_2	CH	X	CH_2	CH	X
CH_2=CH–Be•	+0.018	−0.176	+0.158	−0.076	−0.773	+0.849	−0.089	−0.774	+0.862
CH_2=CH–BH•	+0.095	−0.160	+0.065	+0.008	−0.636	+0.628	−0.009	−0.669	+0.677
CH_2=CH–CH_2•	+0.032	−0.064	+0.032	−0.014	+0.027	−0.014	−0.012	+0.024	−0.012
CH_2=CH–NH•	+0.035	+0.095	−0.131	+0.007	+0.643	−0.649	+0.001	+0.688	−0.688
CH_2=CH–O•	+0.050	+0.218	−0.268	+0.044	+0.996	−1.041	+0.026	+1.037	−1.064
CH_2=CH–Mg•	−0.012	−0.360	+0.372	−0.138	−0.598	+0.737	−0.161	−0.620	+0.782
CH_2=CH–AlH•	+0.063	−0.358	+0.296	−0.042	−0.684	+0.727	−0.060	−0.703	+0.763
CH_2=CH–SiH_2•	+0.059	−0.303	+0.245	+0.002	−0.691	+0.689	−0.007	−0.714	+0.721
CH_2=CH–PH•	+0.082	−0.281	+0.199	+0.033	−0.595	+0.562	+0.023	−0.638	+0.614
CH_2=CH–S•	+0.149	−0.187	+0.038	+0.095	−0.125	+0.031	+0.074	−0.177	+0.104

[a] Based on 6-311G** wave functions.

Table 7. Spin Polarization in Allyl-Type Radicals Using a Mulliken-Type Analysis[a]

	MP2/6-311G**			B3LYP/6-311G**			QCISD/6-311G**		
compd	X	C1	C2	X	C1	C2	X	C1	C2
CH_2=CH–Be•	0.957	−0.923	1.043	0.934	0.068	−0.013	0.940	0.071	−0.020
CH_2=CH–BH•	0.936	−1.113	1.244	0.982	−0.007	−0.009	1.006	−0.029	0.001
CH_2=CH–CH_2•	0.724	−0.305	0.724	0.691	−0.262	0.691	0.746	−0.339	0.746
CH_2=CH–NH•	0.496	−0.244	0.854	0.515	−0.235	0.803	0.529	−0.298	0.881
CH_2=CH–O•	0.039	0.117	0.980	0.292	−0.122	0.911	0.275	−0.168	1.002
CH_2=CH–Mg•	0.925	−0.802	0.928	0.819	0.178	−0.023	0.860	0.159	−0.037
CH_2=CH–AlH•	0.876	−0.959	1.066	0.830	0.067	−0.011	0.864	0.047	−0.008
CH_2=CH–SiH_2•	0.965	0.502	−0.495	0.917	−0.077	0.154	0.993	−0.097	0.130
CH_2=CH–PH•	0.911	−0.091	0.244	0.852	−0.190	0.397	0.931	−0.244	0.390
CH_2=CH–S•	0.773	−0.146	0.414	0.727	−0.179	0.494	0.800	−0.253	0.502

[a] All results were calculated using MP2(full)/6-31G* optimized geometries. There are also small spin populations at the hydrogens.

Table 8. Spin Polarization in Allyl-Type Radicals Derived by Integration[a]

	AIM/B3LYP/6-311G**			AIM/QCISD/6-311G**			QCISD/6-311G**		
compd	X	C1	C2	X	C1	C2	X	C1	C2
$CH_2{=}CH{-}Be^{\bullet}$	0.895	0.101	−0.007	0.900	0.105	−0.013	0.997	0.000	−0.027
$CH_2{=}CH{-}BH^{\bullet}$	0.811	0.079	0.005	0.814	0.076	0.009	0.910	−0.000	0.013
$CH_2{=}CH{-}CH_2^{\bullet}$	0.554	−0.125	0.554	0.573	−0.155	0.573	0.670	−0.203	0.670
$CH_2{=}CH{-}NH^{\bullet}$	0.457	−0.113	0.657	0.452	−0.135	0.687	0.491	−0.182	0.718
$CH_2{=}CH{-}O^{\bullet}$	0.259	−0.030	0.764	0.236	−0.047	0.812	0.268	−0.113	0.872
$CH_2{=}CH{-}Mg^{\bullet}$	0.827	0.156	−0.011	0.868	0.135	−0.022	0.744	0.109	−0.022
$CH_2{=}CH{-}AlH^{\bullet}$	0.766	0.101	0.000	0.794	0.089	0.001	0.563	0.172	0.000
$CH_2{=}CH{-}SiH_2^{\bullet}$	0.699	0.015	0.126	0.729	0.012	0.104	0.737	−0.054	0.110
$CH_2{=}CH{-}PH^{\bullet}$	0.721	−0.068	0.312	0.761	0.034	0.293	0.879	−0.132	0.299
$CH_2{=}CH{-}S^{\bullet}$	0.691	−0.088	0.396	0.750	−0.130	0.383	0.752	−0.149	0.407

[a] The AIM populations were calculated using PROAIMV.[24] The populations in the last columns were obtained by integration of the appropriate regions in 3-D plots of spin density (cf. Figure 3). The small spin populations at the hydrogens are not given.

of the α spin at the heteroatom for all except PH and S where there is an increasing α population at the terminal C and an increase in spin polarization.

The net result is that the odd electron prefers to go to the atom that has the smaller electronegativity. When the terminal atoms have similar electronegativities, they have about equal α spin populations. It can be seen that both stabilization and spin polarization are found with those radicals that have similar electronegativities for the terminal atoms.

The spin polarization values given above are based on a Mulliken-type population analysis, and this type of analysis is known sometimes to give problems.[38] Thus, it seemed desirable to have an independent method for examining the polarization. We have used two approaches. First, the α and β spin populations were separately obtained by integration of the appropriate wave functions over the volume elements defined by Bader's theory of atoms in molecules.[29] The differences between the two spin populations thus obtained are given in Table 8 for both B3LYP and QCISD wave functions in the column marked AIM. Second, it is readily possible to calculate the difference between the α and β spin densities at any point.[39] A 100 × 100 × 100 grid of these differences was calculated about the radical in question, and the result was visualized as a 3-D plot (Figure 3). The excess α spin is indicated by solid contours and the excess β spin is indicated by dashed contours. It can be seen that each atom in the allyl radical is polarized opposite to its neighbors. The extent of spin polarization may be obtained by numerically integrating each of the regions, leading to the values shown in the last columns of Table 8. There is generally good agreement between the spin polarizations calculated via AIM and via integrations of the charge density difference maps. In contrast to the atomic charges, the spin polarizations derived from the Mulliken population analysis (Table 7) are fairly close to those obtained by integration of the wave functions.

Experimentally, spin polarization has been measured for only allyl,[5] 1-oxyallyl,[6] and vinylsilyl[16] radicals. With the former, the α spin populations at the terminal carbons are 0.58 each, and the β spin population at the central carbon is 0.16. This is in very good agreement with the values derived both by the AIM approach and by integrating the regions shown in Figure 3. With the 1-oxyallyl radical, the experimental data give spin populations of 0.7 at the terminal CH_2, 0.2 at the oxygen, and relatively little at the central carbon. The vinylsilyl radical was reported to have a spin population of 0.27 at the terminal carbon, relatively little at the central carbon, and about 0.73 at the silicon. Again, these values are in agreement with the calculated spin polarization.

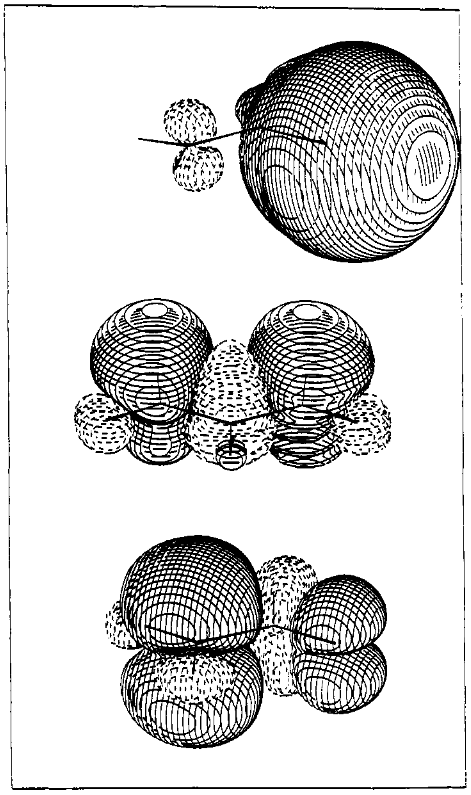

Figure 3. Spin polarization in the $CH_2{=}CH{-}Be^{\bullet}$ radical (upper), allyl radical (middle), and $CH_2{=}CH{-}O^{\bullet}$ radical (bottom). The α spin density is shown with solid contours and the β spin density is shown with dashed contours. The radicals are oriented with a methylene group at the left.

Is the stabilization of allyl radicals directly related to the spin polarization? We have examined this question by comparing the energies for some of these radicals calculated at the UB3LYP and ROB3LYP levels (Table 9). The former is an unrestricted calculation which reproduces the spin polarization, whereas the latter is based on a restricted open-shell formalism that does not permit spin polarization. It can be seen that the difference in energy between the two theoretical levels is essentially constant, despite considerable differences in stabilization energies. Similar energy differences were found with localized radicals. Thus, it appears unlikely that spin polarization contributes much to the stabilization of these radicals.

4. Comparison with Other Allyl-Type Radicals

In their discussion of resonance stabilization of allyl radicals, Feller, Davidson, and Borden concluded that formyloxy (O—

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(37) Cottrell, T. L. *The Strengths of Chemical Bonds*; Butterworths: London, 1958; pp 274 and 276.

(38) Mulliken, R. S.; Politzer, P. *J. Chem. Phys.* **1971**, *55*, 5135. Grier, D. D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3556, and ref 29.

(39) This capability is built into Gaussian-93.

Table 9. Effect of Spin Polarization on Calculated Energies, 6-311+G**

	ROB3LYP[a]	ΔE (kcal/mol)[b]
$CH_2{=}CH{-}CH_2^{\bullet}$	−117.294 45	−2.30
$CH_2{=}CH{-}O^{\bullet}$	−153.218 79	−1.44
$CH_2{=}CH{-}PH^{\bullet}$	−419.958 74	−1.34
$CH_3CH_2^{\bullet}$	−79.183 47	−0.91
$CH_3O^{\bullet}$	−115.085 40	−4.08
$CH_3PH^{\bullet}$	−381.864 99	−0.76

[a] The UB3LYP energies are given in Table 1. [b] Difference in energy between UB3LYP and ROB3LYP calculations.

Table 10. Hydrogen ATom Transfer Reactions

	ΔH, 0 K, kcal/mol		
reaction	B3LYP[a]	G2(MP2)	G2
$O{=}CH{-}OH + CH_3O^{\bullet} \rightarrow O{=}CH{-}O^{\bullet} + CH_3OH$	+5.8	+5.6	+6.1
$CH_2{=}O^{+}{-}CH_3 + C_2H_5^{\bullet} \rightarrow CH_2{=}O^{+}{-}CH_2^{\bullet} + C_2H_6$	−3.3	+0.9	+0.8

		energies[b]		
	ZPE	B3LYP	G2(MP2)	G2
formic acid	20.8	−189.819 00	−189.511 08	−189.516 30
formyloxy radical	10.4	−189.135 06	−188.833 77	−188.839 21
$CH_2{=}O^{+}{-}CH_3$	41.5	−154.154 80	−153.837 49	−153.840 62
$CH_2{=}O^{+}{-}CH_2^{\bullet}$	31.5	−153.486 14	−153.175 24	−153.178 65
$CH_3O^{\bullet}$	22.6	−115.085 77	−114.863 45	−114.867 47
CH_3OH	31.0	−115.757 29	−115.531 82	−115.534 89
$C_2H_5^{\bullet}$	35.5	−79.183 57	−78.968 11	−78.970 17
C_2H_6	44.7	−79.856 23	−79.628 93	−79.630 90

[a] The 6-311G** basis set was used for these calculations. [b] The total energies are given in hartrees and the zero-point energies are given in kcal/mol.

Table 11. 6-311G* Spin Polarization

		B3LYP		QCISD	
compd	atom	Mulliken	AIM	Mulliken	AIM
formyloxy	C	−0.070	−0.001	−0.092	−0.006
($O{=}CH{-}O^{\bullet}$)	H	0.328	0.262	0.348	0.271
	O	0.371	0.369	0.372	0.368
2-oxyallyl	C[a]	0.770	0.634	0.871	0.698
($CH_2{=}O^{+}{-}CH_2^{\bullet}$)	C=	0.496	0.391	0.446	0.338
	O	−0.029	−0.012	−0.170	−0.015

[a] It should be noted that the two C−O bond lengths in the radical are different (ref 13).

CH−O) and 2-oxyallyl ($CH_2{-}O^{+}{-}CH_2$) radicals had little stabilization.[13] Their conclusions are confirmed by the hydrogen atom transfer reactions shown in Table 10. Here, the formation of these radicals was found to be endothermic, indicating destabilization rather than stabilization.

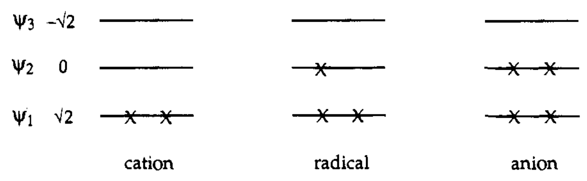
It was also of interest to examine the spin polarization for these radicals. Again, QCISD/6-311G** wave functions were obtained at UMP2/6-31G* geometries. The spin polarization is given in Table 11. In the formyloxy radical, the spin is distributed between the hydrogen and the two oxygens, but there is little odd spin or spin polarization at the central carbon. In the 2-oxyallyl radical, the spin is distributed between the two carbons, but the oxygen has little odd spin or spin polarization.

It can be seen that the requirements for stabilization and for spin polarization are the same: all three atoms forming the allyl radical system should have essentially the same electronegativity. It is not sufficient to be able to write two equivalent resonance structures. What is the special characteristic of allyl-type radicals having three backbone elements with similar electronegativities? The most obvious is that sharing of π electrons between nuclear centers will be more even. In the case of the well-studied hydrogen molecule, optimization of the 1s orbital exponent coefficient leads to a value significantly larger than 1, indicating that the electrons in the overlap region experience a nuclear attraction greater than that for either center alone. This leads to stabilization, and the same should be true for the odd electron in allyl radicals in which the atoms have similar electronegativities. On the other hand, differences in electronegativity will lead the odd electron to be localized on the less electronegative atoms, and there will not be an increase in energy on rotation about the bond to this atom.

5. Comparison with Allyl Cations and Anions

The three allyl systems, cation, radical, and anion, have received much study because they are such common species and are involved in many chemical processes. It was of interest to us to compare the requirements for stabilization of the cation and anion with that for the radical.

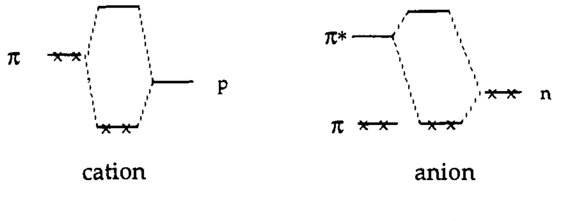
They are commonly related using the Hückel π-electron model, for which the MO energy levels are shown below:



Here ψ_2 is nonbonding, so that in this approximation addition of electrons to allyl cation will not change the total π-energy.

However, this is little more than a mnemonic. When electrons are added to the cation, they repel *both* the σ and the π electrons already present, leading to changes in the energy levels and to charge reorganization which are completely ignored in the Hückel approximation. It was seen in the results presented above that the ability to write two equivalent resonance structures for allyl-type radicals does not assure that stabilization will be found. What are the requirements for stabilization of allyl cations and anions?

The question may also be posed in the context of frontier MO theory (FMO):



The orbital interaction that stabilizes the allyl cation is between a filled and an empty level, and one would expect relatively strong stabilization as long as the energy levels are not too dissimilar, and the interaction matrix element is relatively large. Both requirements are fulfilled for the allyl cation. In contrast to the cation, the lowest energy orbital interaction in the anion would be between two filled levels, and this would not be expected to lead to stabilization. The stabilizing interaction would then be between the lone pair orbital and the considerably higher energy π^* orbital, and it might be expected to give a smaller degree of stabilization.

Before comparing the three types of allyl systems, it seems appropriate to comment on the definition of resonance stabilization since this was a major point in a recent study of these systems by Gobbi and Frenking.[40] Wheland's definition[41] is as follows: "The resonance energy ... is defined as the quantity obtained by subtracting the actual energy of the molecule from that of the most stable contributing structure." The problem with this definition is that no one knows how to calculate the energy of the "most stable contributing structure". In the case of benzene, attempts to apply this definition have led to values of the resonance energy that range from 13 to 55 kcal/mol![42] It seems clear that we must be satisfied with operational definitions.[43] For the allyl systems, the C−C rotational barrier has generally been taken as a measure of the π-stabilization. This is a convenient definition, but of course there are significant changes in the σ system, such as bond lengths, that accompany this rotation, and they also have an energetic consequence. Nevertheless, we shall use this definition in the following discussion.

One might expect allyl cations to be relatively insensitive to structural changes because the cationic site in one resonance structure is a "hole" into which the π-electrons of the double bond can be delocalized. However, if the positive charge is stabilized in some way, it will give a smaller interaction with a π-bond than would an unstabilized cationic center. We have studied the rotational barrier for the allyl cation itself, and we found that at the MP2/6-31G* level, rotation of a terminal methylene led to a hydrogen migration from C2 in order to avoid forming a primary carbocation.[44] A transition structure could be found at the HF/6-31G* level, and although it is not a true transition state, its geometry may be used to estimate the "classical" rotational barrier. It was studied at the G2[15] theoretical level (cation, $E = -116.708\,70$ hartrees; rotated cation, $E = -116.656\,16$ hartrees) and the barrier was found to be 33.0 kcal/mol. The 1,1,3,3-tetramethyl allyl cation, for which rotation of a methylene group gave a true transition state, gave a barrier of 19.8 kcal/mol.[44] Clearly, stabilization of the cationic charge by the methyl group has a considerable effect on the barrier.

The planar allyl cations have their charge dispersed over several atoms, whereas in the rotational transition states, the charge is largely localized at one center. The electrostatic energy of a charged ion depends on its volume, being decreased by an increase in volume. Thus, the electrostatic energy will be increased in the rotated structure, and this is one component of the gas-phase barrier height.[3] In our earlier study,[3] we made a crude estimate of the magnitude of the effect. Subsequently, we have been working on self-consistent reaction field models in order to gain a better estimate of the solvent effect.[45] In the case of the allyl cation, the barrier is reduced by 5.7 kcal/mol to 27.3 kcal/mol on going from the gas phase to a solvent of high dielectric constant. With the tetramethylallyl cation, it is reduced by 1.6 kcal/mol on going to a solvent of high dielectric constant. We consider the barriers found in media of high dielectric constant to be the more appropriate measure of the π-stabilization.

The effect of heteroatom substitution on the stabilization of allyl cations has been examined by Gobbi and Frenking,[46] who found that in the series $CH_2CHXH_2^+$, the calculated C−X rotational barriers decreased from 38 kcal/mol for X = C to 14 kcal/mol when X = Si, 12 kcal/mol when X = Ge, and 7 kcal/mol when X = Sn. Clearly, when the cationic center is at an electropositive atom, the interaction with a π-bond is decreased. Electronegative atoms also reduce stabilization, so that the planar 1-oxyallyl cation ($CH_2{=}CHO^+$) is a transition state, and the lower energy structure has the terminal methylene group rotated ~90°.[47]

The allyl anion itself does have a significant rotational barrier. What is the source of the barrier? The G2 energies of planar and rotated allyl anions are $-117.025\,31$ and $-116.992\,96$ hartrees, respectively, leading to a rotational barrier of 20.3 kcal/mol. When placed in a medium of $\epsilon = 40$, the rotational barrier is calculated to be reduced to 16.7 kcal/mol. The solvent effect is considerably smaller than we had earlier estimated using a crude model, and correspondingly, the π-stabilization energy is considerably larger. Surprisingly, the barrier is markedly reduced by methyl substitution, with the 1,1,3,3-tetramethyl derivative having a rotational barrier of only 8.6 kcal/mol (reduced to 7.0 kcal/mol in a solvent with $\epsilon = 40$).[44]

It is important to note that the stabilization found with the allyl anion also decreases markedly when one or both of the terminal atoms are replaced with an electronegative atom. The carboxylate ion is probably the most studied of these ions, and the acidity of carboxylic acids as compared to alcohols has commonly been attributed to resonance stabilization in the carboxylate ion.[48]

However, more recent studies have shown that this is not the case. This was first suggested by Siggel and Thomas[49] based on the lack of change of the oxygen core ionization potentials on going from a carboxylic acid to its anion, suggesting that the charge density at the oxygens is not much changed on ionization. This was confirmed by several theoretical studies of the charge density distribution in these species[50] in which it was again found that it was not much changed on going from the carboxylic acid to its anion. The two oxygens in the acid already have a large negative charge, whereas the electron population at the acidic hydrogen is small. Further evidence comes from studies of the potential energy and reorganization energy components of the change in energy on going from a carboxylic acid to its anion, where it was found that the latter term (which would include the resonance stabilization) was quite small.[51] The acidity of carboxylic acids may then be related to the strong polarization of the carbonyl group in the sense $C^+{-}O^-$. The positive charge at the carbonyl carbon helps stabilize the negative charge of the carboxylate ion.

This can be confirmed by comparing the acidity of formic

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[40] Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 3275.

[41] Wheland, G. W. *The Theory of Resonance*; Wiley: New York, 1955; p 75.

[42] Cf.: Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166. Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1965; pp 56 and 66.

[43] In this connection, it is worth noting Pauling's statement: "The theory of resonance in chemistry is essentially a qualitative theory, which like the classical structural theory, depends for its successful application largely upon a chemical feeling that is developed through practise." Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 220.

[44] Foresman, J. B.; Wong, M. W.; Wiberg, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 2220.

[45] Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776. Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Chem. Phys.* **1991**, *95*, 8991. Wiberg, K. B.; Wong, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 1078. Foresman, J.; Keith, T.; Wiberg, K. B.; Frisch, M. J. To be submitted for publication.

[46] Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9287.

[47] The rotated oxyallyl cation was found at the MP2/6-31+G* level to have a bridged structure.

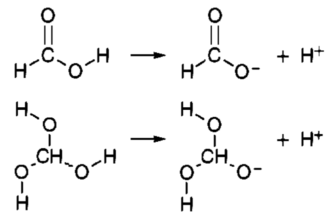
[48] Cf. ref 35, p 345, and most elementary organic chemistry texts. It should be noted that Wheland recognized the importance of electrostatic factors in this case and concluded that it was not possible at that time (1955) to estimate the relative importance of electrostatic and resonance contributions.

[49] Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360.

[50] Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872. Siggel, M. R. F.; Streitwieser, A.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022. Thomas, T. D.; Siggel, M. R. F.; Streitwieser, A. *J. Mol. Struct.* **1988**, *165*, 309. Thomas, T. D.; Carroll, T. X.; Siggel, M. R. F. *J. Org. Chem.* **1988**, *53*, 1812.

[51] Ji., D.; Thomas, T. D. *J. Phys. Chem.* **1994**, *98*, 4301.

acid with that of orthoformic acid.[52]



We have found that a double bonded oxygen has essentially the same effect on the charge at a carbonyl carbon as two single bonds to oxygen.[53] Then, the ionization of orthoformic acid would be comparable to that of formic acid as far as the charge at the carbon is concerned. A calculation of the gas phase acidity of orthoformic acid at the G2 theoretical level gave 352.6 kcal/mol, as compared to 381.4 kcal/mol for methanol and 345.7 kcal/mol for formic acid. Thus, 80% of the increased acidity of formic acid may be attributed to the charge at the carbon. One might expect that formic acid would be somewhat more acidic than orthoformic acid since in its anion it can distribute the negative charge between two oxygens, thus reducing its electrostatic energy.

A series of heterosubstituted allyl anions have been studied by us[54] and by Gobbi and Frenking.[40] With both series of compounds, substitution led to a marked reduction in resonance stabilization. Only in the case of the allyl anion itself is a high degree of stabilization found.

It can be seen that the stabilization of allyl systems is rather fragile and can be markedly reduced by electronegative substituents that can stabilize negative charges in the case of the anion, by more or less electronegative substituents in the case of allyl radicals and by groups that stabilize positive charges in allyl cations. In all cases, stabilization is found mainly in the cases where the three atoms of the allyl system have similar electronegativities. This will tend to maximize the π-charge distribution between the nuclei and lead to the maximum decrease in their potential energy. Any substitution that affects this balance in charge distribution will decrease the stabilization, as is found to be the case.

6. Conclusions

In allyl radicals, the odd electron prefers to be found at the less electronegative atom, and when there is a significant difference in electronegativity, there is little spin polarization and little stabilization of the allyl radical. When all three atoms forming the allyl radical backbone have similar electronegativities, the radical becomes stabilized, the odd electron is shared between the terminal atoms, and the central atom becomes spin polarized in the opposite sense to the terminal atoms. However, the spin polarization does not appear to contribute much to the net stabilization. The requirement for allyl radical π stabilization is that all three atoms forming the allyl system must have similar electronegativities.

Allyl cations, radicals, and anions are often treated together in discussions of "resonance stabilization". However, stabilization is somewhat different for the cations and anions. Allyl cations are stabilized by the delocalization of the π-bond density into a region of lower potential energy, the empty p orbital. Allyl anions and related compounds of the type $CH_2{=}CH{-}X$ where X has a lone pair have two possible modes of stabilization. In the case of vinyl thiol we have shown that the main interaction is a repulsion between the S lone pair and an electron in the π-orbital at the adjacent carbon.[1d] This leads to polarization of the C=C π bond and an attractive interaction between the double bond and the lone pair. A second type of interaction is charge donation from a lone pair to the terminal atom of the double bond, such as with thioamides.[55]

The maximum charge donation is found with the allyl anion, where the two terminal carbons have equal charge. This leads to 60% of the stabilization found with an allyl cation. Any substitution that removes the symmetry of the allyl anion will markedly reduce its π stabilization.

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Supplementary Material Available: Tables giving the 6-311G* energies and energy differences (4 pp). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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