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Resonance Interactions in Acyclic Systems. 2. Y-Conjugated Anions and Cations

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Abstract: The first and second ionization energies of isobutene, acetone, acetic acid, and carbonic acid were calculated at the MP3/6-311++G**//6-31G* level giving values that agreed with the available experimental data. The first ionization energy decreased by 21 kcal/mol for each of the first two replacements of CH_2 by O but decreased by only 10 kcal/mol for the third replacement. The second ionization energy was high and was the same for the first three compounds. It decreased for the third replacement of CH_2 by O. It was concluded that the electronegativity of the terminal atoms determines the ionization energies, and that there was no evidence for Y aromaticity in the gas phase. In solution, the anions formed ion pairs or triplets with lithium, and this markedly reduced the energies of formation. The energies of reaction of isobutene with lithium hydride were calculated, and both the first and second reactions were found to be exothermic. The cations formed by the loss of one or two hydride ions from isobutene, and by the addition of a proton to guanidine, also were studied. The allyl cations had significant resonance stabilization, but no special stabilization was found for the dication. Guanidinium ion was found to have little if any resonance stabilization. The origin of the basicity of guanidine is discussed.

One of the remarkable observations in carbanion chemistry is the facile reaction of butyllithium with the monoanion derived from isobutene to give the dianion.[1] This and related observations have received considerable attention and have been attributed either to "Y-aromaticity"[2,3] or to internal coulombic stabilization resulting from charge alternation.[4] Both viewpoints have recently been reviewed.[3,4]

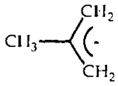
In our study of the formation of allyl anions from their neutral precursors, we found it useful to examine the effect on the ionization energy of replacing the terminal carbons by NH or O.[5] Here, it was found that the replacement of one CH_2 by NH reduced the ionization energy by 12 kcal/mol, and replacement of one CH_2 by O reduced the ionization energy by 23 kcal/mol. Further, the effects were additive.

We have now examined the replacement of carbons in isobutene and the allyl anions[6] derived from it by oxygen. In each case, the geometry was optimized with use of the 6-31G* basis set,[7] and then the MP3/6-311++G** energy was obtained at that geometry. This flexible basis set, which is effectively triple-ζ and includes both diffuse and polarization functions at all atoms, was found to give ionization energies in good accord with the experimental data for the allyl anions.[5] The energies are given in Table I, and the structural parameters are given in Table II. In the case of methallyl anion, two rotamers of the methyl group were examined (**1a** and **1b**) and were found to have essentially the same energy.

The ionization energies, which may be obtained from the data in Table I, are summarized in Table III. There was a considerable change in calculated ionization energies on going from 6-31G* to 6-311++G** showing the necessity of using a flexible basis set in studying these reactions. The MP2 correction for electron correlation overcorrected as is often found to be the case.[8] The MP3 values were close to RHF, and in the earlier related study, the MP4 correction had only a small effect.[5] It was not calculated in the present case because of the size of some of the systems being studied. In order to compare the calculated values with experimental data,[9] it was necessary to correct them for the loss of zero-point energy on ionization, corresponding to the loss of one X-H stretching mode and two X-H bending modes, where X is C or O. The zero-point energy changes were assumed to be the same as for the closely related systems we studied previously,[5] leading to the calculated ΔH values in the table. They are in quite good agreement with experiment.

It is easier to visualize the results by an examination of Figure 1, which shows the ionization energies as a function of the number of oxygens. It can be seen that the first ionization energy changed by 21 kcal/mol for each of the first two replacements of C by O, but that the third replacement decreased the energy by only 10 kcal/mol. In the second ionization step, the first two replacements of C by O had no effect on the ionization energy, but the third replacement decreased the energy by 16 kcal/mol.

These energy changes may readily be understood by examining the ions that are formed. The first ionization step gives the following ions: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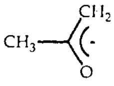
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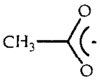
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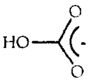
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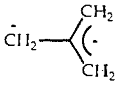
Here, the first three ions are related by replacing a carbon in an allyl anion by oxygen, and as noted previously, the electronegativity of oxygen results in a reduced relative energy. However, with the last ion, the only effect is derived from the replacement of a nonreacting CH_3 by a nonreacting OH. It is not surprising that this gives a smaller effect on the ionization energy.

The ions formed in the second ionization step are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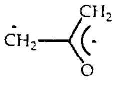
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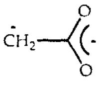
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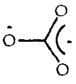
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The first three ions are formed by removing a proton from a methyl group, and the energy change is independent of the rest of the

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[1] Klein, J.; Brenner, S. *J. Am. Chem. Soc.* **1969**, *91*, 3094.

[2] Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.

[3] Agranat, I.; Skanke, A. *J. Am. Chem. Soc.* **1985**, *107*, 867. Cf.: Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1982**, 709. Inagaki, S.; Kawata, H.; Hirabayashi, Y. *J. Org. Chem.* **1983**, *48*, 2928.

[4] Klein, J. *Tetrahedron* **1983**, *39*, 2733; **1988**, *44*, 503.

[5] Wiberg, K. B.; Breneman, C.; LePage, T. *J. Am. Chem. Soc.* In Press.

[6] Theoretical studies of the trimethylenemethyl dianion at the 6-31G level have been reported in ref 3. The rotational barrier was found to be 19 kcal/mol, essentially the same as for allyl anion. The latter has been attributed largely to electrostatic destabilization of the more charge localized rotated form (ref 5).

[7] 6-31G*: Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217. 6-311G*: Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. 6-31+G*: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *4*, 294.

[8] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 278ff.

[9] Lias, S. G.; Bartmess, J. E.; Liebman, J. E.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas Phase Ion and Neutral Thermochemistry*; American Institute of Physics: New York, 1988.

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Table I. Energies of Anions Formed by Proton Loss, H

	6-31G*	6-311++G**(6D)		
compd	RHF	RHF	MP2	MP3
isobutene	−156.110 67	−156.153 37	−156.752 50	−156.794 63
methallyl anion **1a**[a]	−155.430 85	−155.500 10	−156.114 52	−156.147 76
methallyl anion **1b**[b]	−155.430 78	−155.500 03	−156.114 30	−156.147 55
trimethylenemethyl dianion **2**	−154.547 23	−154.672 36	−155.300 20	−155.323 82
acetone	−191.962 23	−192.017 51	−192.662 24	−192.686 70
enolate anion **6**	−191.323 03	−191.397 83	−192.056 58	−192.072 16
enolate dianion **4**	−190.445 06	−190.573 34	−191.244 98	−191.251 17
acetic acid	−227.810 65	−227.883 84	−228.576 85	−228.574 00
acetate anion **5**	−227.225 06	−227.300 07	−228.011 06	−228.009 19
acetate dianion **6**	−226.349 94	−226.482 24	−227.198 16	−227.186 89
carbonic acid	−263.647 48	−263.738 38	−264.477 77	−264.469 74
bicarbonate anion **7**	−263.078 61	−263.179 01	−263.927 62	−263.910 84
carbonate dianion **8**	−262.250 60	−262.385 69	−263.143 42	−263.116 18

[a] One methyl hydrogen perpendicular to the plane of the carbon atoms. [b] One methyl hydrogen in the plane of the carbon atoms.

Table II. Calculated Structures, 6-31G*[a]

compd	unit	value
isobutene	$r(\mathrm{C{=}C})$	1.321
	$r(\mathrm{C{-}C})$	1.508
	$\angle \mathrm{C_1C_2C_3}$	122.3
methallyl anion **1a**	$r(\mathrm{C_1{-}C_2})$	1.530
	$r(\mathrm{C_2{-}C_3})$	1.384
	$\angle \mathrm{C_1C_2C_3}$	115.1
methallyl anion **1b**	$r(\mathrm{C_1{-}C_2})$	1.529
	$r(\mathrm{C_2{-}C_3})$	1.385
	$r(\mathrm{C_2{-}C_4})$	1.382
	$\angle \mathrm{C_1C_2C_3}$	114.9
	$\angle \mathrm{C_1C_2C_4}$	115.2
methallyl dianion **2**	$r(\mathrm{C{-}C})$	1.431
	$\angle \mathrm{CCC}$	120.0
acetone	$r(\mathrm{C{=}O})$	1.192
	$r(\mathrm{C{-}C})$	1.513
	$\angle \mathrm{OCC}$	121.7
etnolate anion **3**	$r(\mathrm{C{-}O})$	1.252
	$r(\mathrm{C_2{-}C_3})$	1.371
	$r(\mathrm{C_3{-}C_4})$	1.552
	$\angle \mathrm{OC_3C_2}$	128.7
	$\angle \mathrm{OC_3C_4}$	115.5
enolate dianion **4**	$r(\mathrm{C{-}O})$	1.291
	$r(\mathrm{C{-}C})$	1.433
	$\angle \mathrm{OCC}$	119.6
acetic acid	$r(\mathrm{C{=}O})$	1.187
	$r(\mathrm{C{-}O})$	1.332
	$r(\mathrm{C{-}C})$	1.502
	$\angle \mathrm{OCC}$	125.8
	$\angle \mathrm{OCO}$	122.4
acetate anion **5**	$r(\mathrm{C{-}C})$	1.554
	$r(\mathrm{C{-}O_1})$	1.233
	$r(\mathrm{C{-}O_2})$	1.235
	$\angle \mathrm{CCO_1}$	116.0
	$\angle \mathrm{CCO_2}$	114.5
acetate dianion **6**	$r(\mathrm{C{-}O})$	1.283
	$r(\mathrm{C{-}C})$	1.437
	$\angle \mathrm{C{-}C{-}O}$	121.4
carbonic acid	$r(\mathrm{C{=}C})$	1.188
	$r(\mathrm{C{-}O})$	1.315
	$\angle \mathrm{O{=}CO}$	125.1
bicarbonate **7**	$r(\mathrm{C{-}O_1})$	1.224
	$r(\mathrm{C{-}O_2})$	1.219
	$r(\mathrm{C{-}O_3})$	1.401
	$\angle \mathrm{O_1CO_2}$	132.0
	$\angle \mathrm{O_1CO_3}$	113.5
carbonate **8**	$r(\mathrm{C{-}O})$	1.285
	$\angle \mathrm{OCO}$	120.0

[a] The lengths are given in Å and the angles in deg. The numbering of the atoms is shown in Table V.

molecule. However, in the formation of carbonate ion, the proton is removed from oxygen, and consequently the ionization energy is reduced.

It can be seen that the energy changes are determined solely by the electronegativity of the groups at the terminal positions,

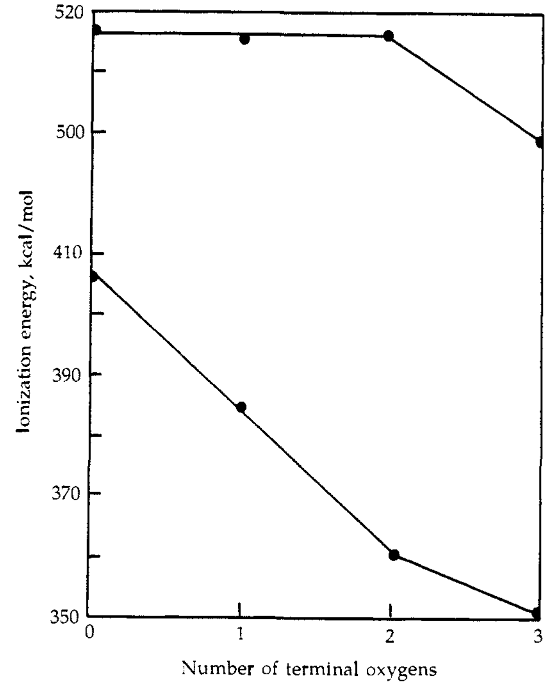
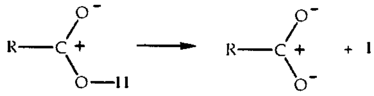


Figure 1. Ionization energies as a function of the number of terminal oxygens. The lower line is for the first ionization step, and the upper line is for the second step.

and there is no need to postulate resonance stabilization. This is in good accord with conclusions that have been reached for allyl anions.[5] For example, with carboxylic acids, the ionization process might best be written as[10]



This would be in accord with the very small change in electron population at the oxygens as a result of ionization and the strong polarization of carbonyl groups. As might be expected the second ionization energies were considerably larger than the first, as has been observed in solution with carbonic acid (first $pK_a = 3.7$, second $pK_a = 10.3$).[11]

In view of these results, how does one rationalize the experimental observation of the ease of forming the dianion from isobutene? Theoretical studies by Streitwieser et al.[12] and by Schleyer

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(10) Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360. Siggel, M. R.; Streitwieser, A., Jr.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022. Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.

(11) Cotton, F. A.; Wilkinson, G. *Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 1988; p 245.

Table III. Energy Changes on Ionization (kcal/mol)

	6-31G*	6-311++G** (6D)			ΔH	
reaction	RHF	RHF	MP2	MP2	est[a]	obs
isobutene → anion	426.6	409.9	400.3	405.9	395	397 ± 3
anion → dianion	554.5	519.4	511.0	517.0		
acetone → anion	401.1	388.8	380.1	385.6	375	369 ± 3
anion → dianion	550.9	517.4	509.3	515.2		
acetic acid → anion	367.5	361.3	355.0	360.7	352	349 ± 3
anion → dianion	549.1	518.2	510.1	516.0		
carbonic → bicarbonate	357.0	351.0	345.2	350.7	342	
bicarbonate → carbonate	519.6	497.8	492.1	498.6		

[a] Derived from the MP3/6-311++G** energies by correction for zero-point energy differences (11 kcal/mol for cleavage of a CH bond and 9 kcal/mol for the cleavage of an OH bond).

Table IV. Energies of Lithio Derivatives

(a) Total Energies, H

	6-31G*	6-311G** (6D)		
compd	RHF	RHF	MP2	MP3
isobutene	-156.110 67	-156.151 83	-156.749 40	-156.791 74
2-methylallyllithium	-162.955 22	-162.999 28	-163.610 94	-163.646 25
dilithioisobutene	-169.802 11	-169.848 32	-170.473 80	-170.502 67
lithium hydride	-7.980 87	-7.985 86	-8.008 71	-8.014 22
hydrogen	-1.126 83	-1.131 52	-1.159 15	-1.165 01

(b) Energy Changes, kcal/mol

	6-31G*	6-311G**		
reaction	RHF	RHF	MP2	MP3
isobutene + LiH → 2-methylallyllithium + H_2	+6.0	+4.3	-7.5	-3.3
2-methylallyllithium + LiH → dilithio + H_2	+6.8	+3.3	-8.3	-4.5

et al.[13] have shown that dilithiopropene and related compounds adopt bridged structures that maximize coulombic attraction between the lithium cations and the anion. It appeared likely that the same would be true with dilithioisobutene. The geometries of the monolithio and dilithio derivatives of isobutene were optimized with use of the 6-31G* basis set, and the energies were calculated at the MP3/6-311G** level. The structures are shown in Figure 2, and the energies are given in Table IV. They were shown to be true minima by calculating the vibrational frequencies at the 6-31G* level. No imaginary frequencies were found. The lowest calculated frequencies were 132 cm^{-1} for the monolithio compound and 159 cm^{-1} for the dilithio compound.

The energy changes for the following reactions were calculated with these data:

$$(CH_3)_2C{=}CH_2 + LiH \rightarrow CH_3C(CH_2)_2^- \, Li^+ + H_2$$

$$CH_3C(CH_2)_2^- \, Li^+ + LiH \rightarrow C(CH_2)_3^{2-} \, 2Li^+ + H_2$$

The calculated energy changes were significantly affected by the correction for electron correlation, and with the MP3/6-311G** energies, the first reaction was calculated to have $\Delta E = -3.3$ kcal/mol and the second to have $\Delta E = -4.5$ kcal/mol. The two energy changes were exothermic and were now very close. This accounts for the observed ease of formation of the dilithio compound. The structures (Figure 2) were those that will maximize the coulombic attraction of the lithium cation(s) for the anions. It seems clear that the formation of the dilithio compounds has little if anything to do with "Y-aromaticity".

Charge Distribution. On the basis of the charge distribution derived from the Mulliken population analysis, it has been suggested that the isobutene dianion is stabilized by an attractive coulombic interaction between the central carbon with a positive charge and the terminal carbons bearing a negative charge.[4] However, Both Mulliken[14] and others[15] have noted the deficiency in the population analysis which uses an arbitrary division of charge density between atoms and is basis set dependent.

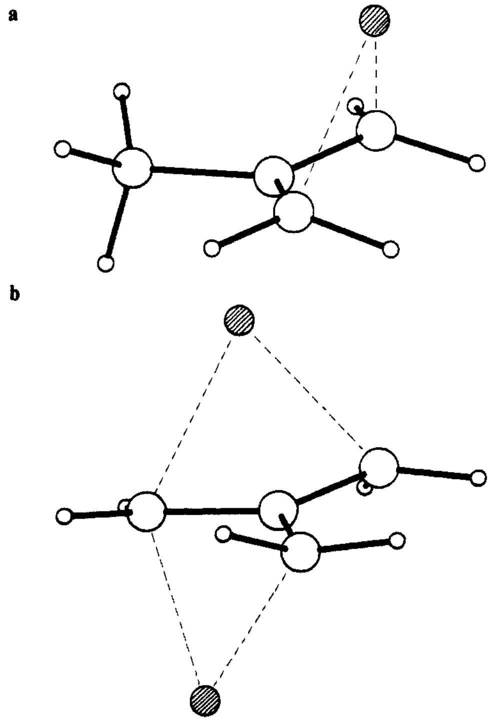

Figure 2. Structures of lithio derivatives of isobutene: (a) the monolithio derivative; (b) the dilithio derivative. The lithiums are shown shaded.

This is well illustrated by the central carbon atom of isobutene. The use of the 6-31G* basis set led to a Mulliken population of 5.892 e, corresponding to a charge of +0.108. With the larger basis set, the population decreased to 4.989 e, corresponding to

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(12) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. Kost, D.; Klein, J.; Streitwieser, A., Jr.; Schriver, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922.

(13) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355. Schleyer, P. v. R.; Kos, A. J.; Kaufman, E. *J. Am. Chem. Soc.* **1983**, *105*, 7617. Kos, A. J.; Stein, P.; Schleyer, P. v. R. *J. Organomet. Chem.* **1985**, *280*, C1.

(14) Mulliken, R. S.; Politzer, P. *J. Chem. Phys.* **1971**, *55*, 5135.

(15) Grier, D. L.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 3556 and references therein.

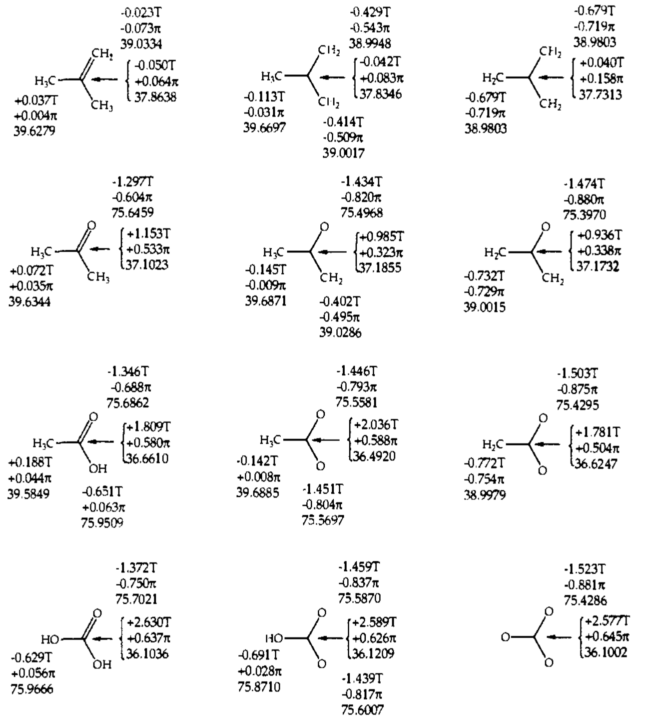

Figure 3. Atomic charges and energies derived via numerical integration for the anions and their parents. The first value (*T*) is the total charge, the second (π) is the charge for the π system, and the third is the kinetic energy, which is minus the total energy for the group or atom. In the case of methallyl anion, conformer **1b** is shown.

a charge of 1.011! Neither charge is reasonable. An sp^2 hybridized carbon is more electronegative than an sp^3 hybridized carbon, and so there should be a drift of charge density from the methyl group to the central carbon, and it should have a small negative charge.

A more satisfactory procedure makes use of Bader's theory of atoms in molecules.[16] Here, zero-flux surfaces are located which separate pairs of bonded atoms. The collection of these surfaces will serve to separate a molecule into a set of atomic domains. Integration of the charge density within one of these domains gives the electron population for the given atom, and similarly, integration of the kinetic energy gives the atomic kinetic energy (T_Ω) that is directly related to the total energy of the atoms ($E_\Omega = -T_\Omega$).

The results of this analysis for the anions are given in Table V. As expected, the electron population at the central carbon of isobutene was 6.050 e, corresponding to a charge of −0.050. The total population for the methyl group was 8.963 e, leading to a small positive charge, +0.037. The group charges for the anions and their parents are summarized in Figure 3.

The monoanion of isobutene again had a small negative charge at the central carbon, and most of the negative charge was at the methylene groups (av −0.422). However, some of the negative charge appeared at the methyl group (−0.113). Finally, with the dianion, the central carbon had only a small positive charge (+0.040) and the methylene groups bore essentially $^2/_3$ of a negative charge each (−0.679). These results do not support the idea of internal coulombic stabilization. It is interesting to note that the hydrogens bore a considerable part of the negative charge in the anions. This is in accord with simple electrostatic concepts, in which an ion will try to put the charge on as large a volume element as possible in order to reduce the electrostatic energy.

In the case of acetone, the carbonyl group was strongly polarized C^+–O^- as is usually found with this group.[17] The charge resulted from two factors, both related to the difference in electronegativity between carbon and oxygen. The more electronegative oxygen will cause some shift in charge density from the carbon to the oxygen. This will, in turn, cause the bond critical point to move toward the carbon. The zero-flux surfaces pass through the critical point, and as a result the "size" of the oxygen in the direction of the carbon increases. The combination of the charge shift and the increased size leads to the relatively large charges assigned to carbon and oxygen.

Turning to the anions derived from acetone (Figure 3), it can be seen that the charge at the terminal carbon was not much different than that found for the isobutene derived ions. However, it was adjacent to a more electron deficient carbon, resulting in greater internal coulombic stabilization. The deprotonation of acetate ion again led to charges in the terminal carbon that were similar to those for the dianions derived from isobutene and acetone, and the increased stabilization of acetate was in part a result of the greater electron deficiency at the central carbon. It can be seen that the internal coulombic stabilization originally proposed for the isobutene dianion is actually found in the anions derived from acetone and acetic acid.

The π-electron populations for each of the atomic regions also are given in Table V and Figure 3. Some polarization of the π-charge is seen with the trimethylenemethyl dianion where the central carbon has a small positive π-charge. It should be noted that whereas the full atomic charges are well defined as the atomic number less the calculated electron population, the π-charges are formal charges based on "normal" populations of 2 for each CH_3 or OH group and 1 for each atom involved with a double bond. The large change in π-charge for the hydroxyl oxygen in the ionization of acetic acid resulted from this definition. It can be seen from Table V that the π-populations at the two oxygens were about the same in acetic acid and in acetate ion.

Energies of Monocation and Dications. In our previous study of allyl cations and anions, the resonance stabilization of the cations was found to be much more important than that for the anions.[5] The difference had a simple origin. In allyl cation, the π-electrons may be distributed one per C–C bond, minimizing electron repulsion. In the anion, however, the additional two electrons will result in an increase in electron repulsion that will markedly reduce the delocalization energy.

The energies of the cations derived by removing one[18] or two hydride ions from isobutene are given in Table VI. For comparison, the energies of guanidine, the guanidinium ion,[19] and some related compounds were calculated, and these data also are included in the table. In our previous study, the rotational barrier for allyl cation was 34.4 kcal/mol at the MP3/6-311++G**//6-31G* level. The barrier for methallyl cation was about the same (33.3 kcal/mol). We have proposed that these barriers for the allyl cations are composed of about half from loss of resonance stabilization and half from the increase in electrostatic energy as the volume associated with the charge is decreased.[5]

The energy of forming the dication was, as expected, quite high. Of more direct interest, the calculated rotational barrier was found to be only 20 kcal/mol, considerably smaller than that for the monocation. A large part of this barrier must be attributed to the increase in electrostatic energy caused by the localization of charge in the rotated ion.[5] This suggests that the dication does not have much additional stabilization despite its "Y-conjugation". Rotation of one methylene group would still leave an allyl system, and so there should not be much loss of resonance stabilization.

The electron populations for the monocations and dications are given in Table VII, and the charges derived from the populations are summarized in Figure 4. In methallyl cation, a considerable part of the positive charge was borne by the methyl group, but

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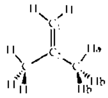
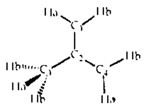
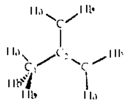
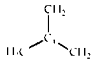
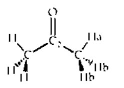
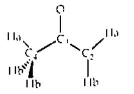
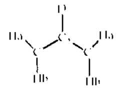
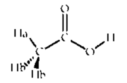
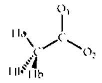
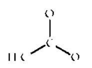
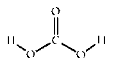
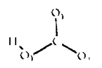
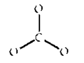
(16) Bader, R. F. W.; Nguyen-Dang, *Adv. Quantum Chem.* **1981**, *14*, 63. Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893. Bader, R. F. W. *J. Chem. Phys.* **1986**, *85*, 3133. Bader, R. F. W. *Acc. Chem. Res.* **1985**, *9*, 18.

(17) Slee, T.; Larouche, A.; Bader, R. W. F. *J. Phys. Chem.* **1988**, *92*, 6219.

(18) For a previous theoretical study of the methallyl cation (STO-3G) see: Mayr, H.; Forner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 1032. For a previous theoretical study of the trimethylenemethyl dication (6-31G) see ref 3.

(19) For a previous theoretical study of the guanidinium ion see: Sapse, A. M.; Massa, L. J. *J. Org. Chem.* **1980**, *45*, 719. Herzig, L.; Massa, L. J.; Santoro, A.; Sapse, A. M. *J. Org. Chem.* **1981**, *46*, 2330. They found a rotational barrier (6-31G) of 14.7 kcal/mol and an experimental barrier of 13 kcal/mol.

Table V. Electron Populations for Anions and Their Parents, 6-311++G**

compd	atom	n_π	n_T	T^a
isobutene	C_1	1.0006	5.9700	37.7712
	H	0.0360	1.0263	0.6311
	C_2	0.9356	6.0500	37.8638
	C_3	0.9130	5.8525	37.7176
	Ha	0.0274	1.0345	0.6377
	Hb	0.5276	1.0382	0.6363
	sum	5.9994	31.9994	156.1530
				(156.1534)
methallyl anion **1a**	C_1	0.8356	5.8617	37.7071
	Ha	0.5856	1.0833	0.6511
	Hb	0.2256	1.0848	0.6555
	C_2	0.9442	6.0447	37.8329
	C_3	1.4082	6.1750	37.6869
	Hc	0.1086	1.1284	0.6578
	Hd	0.0750	1.1183	0.6537
	sum	6.0004	32.0029	155.4989
				(155.5001)
methallyl anion **1b**	C_1	0.8954	5.8608	37.7077
	Ha	0.0354	1.0874	0.6570
	Hb	0.5502	1.0824	0.6525
	C_2	0.9166	6.0421	37.8346
	C_3	1.3908	6.1805	37.6839
	Ha	0.0798	1.1301	0.6579
	Hb	0.0722	1.1185	0.6530
	C_4	1.3602	6.1695	37.6893
	Ha	0.0800	1.1263	0.6582
	Hb	0.0686	1.1177	0.6542
	sum	5.9994	31.9977	155.5008
				(155.5000)
trimethylenemethyl dianion **2**	C_1	0.8422	5.9605	37.7313
	C_2	1.5228	6.3438	37.6617
	H	0.0982	1.1675	0.6593
	sum	5.9998	31.9969	154.6722
				(154.6724)
acetone	O	1.6036	9.2966	75.6459
	C_2	0.4666	4.8469	37.1023
	C_3	0.9144	5.9017	37.7666
	Ha	0.0240	0.9899	0.6176
	Hb	0.5132	1.0181	0.6251
	sum	5.9998	31.9991	192.0170
				(192.0175)
enolate anion **3**	O	1.8198	9.4344	75.4968
	C_2	1.3576	6.1713	37.7230
	Ha	0.0666	1.1003	0.6451
	Hb	0.0706	1.1304	0.6605
	C_3	0.6774	5.0152	37.1855
	C_4	0.8808	5.9059	37.7370
	Ha	0.0290	1.0616	0.6449
	Hb	0.5496	1.0887	0.6526
	sum	6.0008	31.9965	191.3980
				(191.3978)
enolate dianion **4**	O	1.8802	9.4743	75.3970
	C_3	0.6618	5.0642	37.1732
	C_2	1.5326	6.3937	37.6879
	Ha	0.1002	1.1589	0.6514
	Hb	0.0964	1.1793	0.6622
	sum	6.0004	32.0023	190.5732
				(190.5733)
acetic acid	C(Me)	0.9316	5.8490	37.7398
	Ha	0.0244	0.9844	0.6167
	Hb	0.4998	0.9891	0.6142
	C	0.4202	4.1914	36.6610
	=O	1.6876	9.3458	75.6867
	O	1.9274	9.2982	75.6225
	H	0.0094	0.3528	0.3284
	sum	6.0002	31.9998	227.8835
				(227.8838)
acetate anion **5**	C(Me)	0.8828	5.9076	37.7425
	Ha	0.0292	1.0785	0.6514
	Hb	0.5400	1.0778	0.6473
	C	0.4118	3.9640	36.4920
	O_1	1.7926	9.4462	75.5581
	O_2	1.8042	9.4511	75.5697
	sum	6.0006	32.0030	227.3083
				(227.3081)
acetate dianion **6**	C_1	1.5526	6.4235	37.6847
	H	0.1008	1.1744	0.6566
	C_2	0.4952	4.2195	36.6247
	O	1.8750	9.5032	74.4295
	sum	5.9994	31.9982	226.4816
				(226.4822)
carbonic acid	C	0.3628	3.3703	36.1036
	=O	1.7498	9.3716	75.7021
	O	1.9344	9.2906	75.6453
	H	0.0092	0.3386	0.3213
	sum	5.9998	32.0003	263.7389
				(263.7384)
bicarbonate anion **7**	C	0.3744	3.4112	36.1209
	O_1	1.8372	9.4591	75.5870
	O_2	1.8172	9.4394	75.6007
	O_3	1.9590	9.2885	75.5091
	H	0.0130	0.4021	0.3619
	sum	6.0008	32.0003	263.1796
				(263.1790)
carbonate dianion **8**	C	0.3552	3.4229	36.1002
	O	1.8810	9.5231	75.4286
	sum	5.9982	31.9922	262.3860
				(262.3857)

[a] The electron populations are given for the π-system (n_π) and for all the electrons (n_T). The kinetic energies (T) were corrected for the virial defect found in the RHF calculations and sum to a value close to the negative of the total energy (E). The values of $-E$ are given in parentheses.

its π-charge was small. The central carbon also bore part of the positive charge, but again its π-charge was small. The same was true of the dication.

The protonation of guanidine to form guanidinium ion may be examined in the same fashion. In order to have another system for comparison, the energies of propanimine (**9**) and propaniminium ion (**10**) also were calculated. The protonation of guanidine was calculated to be only 10 kcal/mol more exothermic than that of propanimine. If guanidinium ion were strongly resonance stabilized, one might reasonably expect a considerably larger difference in energy. Some differences should be expected since guanidinium ion would have its charge spread over three equivalent groups, leading to a lower electrostatic energy than for propaniminium ion. Another indication of the low resonance stabilization of guanidinium ion was the small rotational barrier, 14 kcal/mol, which was in good agreement with previous calculations and experimental observations.[19] Most of the barrier probably resulted from the decrease in the volume over which the charge is distributed when one NH_2 group was rotated.[5]

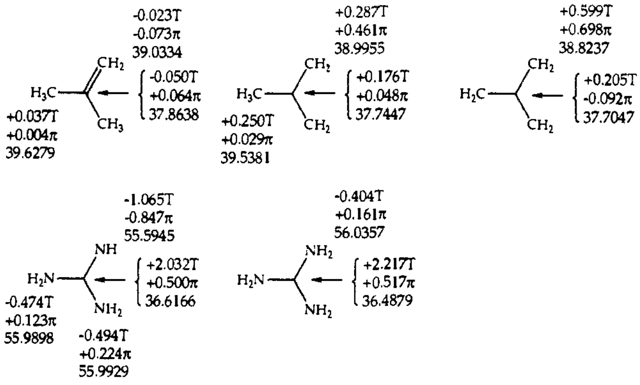


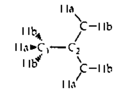
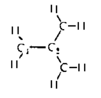
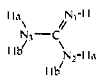
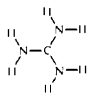
Figure 4. Atomic charges and energies derived via numerical integration for the cations and their parents.

The charge distributions for guanidine and guanidinium ion (Table VII and Figure 4) show that the nitrogens do not change

Table VI. Formation of Cations

	6-31G*	6-311++G** (6D)		
compd	RHF	RHF	MP2	MP3
(a) Energies of Cations and Related Compounds, H				
isobutene	−156.110 67	−156.153 37	−156.752 50	−156.794 63
methallyl cation	−155.235 17	−155.273 53	−155.824 68	−155.863 61
methallyl dication	−154.138 75	−154.174 76	−154.655 80	−154.696 81
methallyl cation, rot. 90°	−155.183 72	155.223 43	−155.769 04	−155.810 54
methallyl dication, rot. 90°	−154.101 89	−154.138 47	−154.623 70	−154.664 67
guanidine	−204.119 94	−204.194 18	−204.879 89	−204.895 91
guanidinium ion	−204.521 52	−204.593 08	−205.262 29	−205.284 05
guanidinium ion, rot. 90°	−204.496 99	−204.568 84	−205.241 10	−205.262 60
propanimine	−172.115 99	−172.166 16	−172.794 48	−172.828 21
propaniminium ion	−172.497 52	−172.548 12	−173.161 84	−173.200 80
H^-	−0.422 44	−0.486 96	−0.505 65	−0.510 70
(b) Energies of Ionization, kcal/mol				
isobutene → methallyl cation	284.3	246.5	264.9	263.8
methallyl$^+$ → methallyl dication	422.9	383.9	416.2	414.9
guanidine + H^+ → guanidinium cation	252.0	250.3	240.0	243.6
propanimine + H^+ → ion	239.4	239.7	230.5	233.8
(c) Rotational Barriers, kcal/mol				
methallyl cation	32.3	31.4	34.9	33.3
methallyl dication	23.1	22.8	20.1	20.2
guanidinium ion	14.1	15.2	13.3	13.5

Table VII. Atom Properties of Cations, 6-311++G**

compd	atom	n_π	n_T	T[a]
methallyl cation	C_1	0.9590	5.8387	37.7066
	Ha	0.6296	0.9623	0.6059
	Hb	0.1910	0.9747	0.6128
	C_2	0.9522	5.8236	37.7447
	C_3	0.5152	5.9951	37.8645
	Ha	0.0106	0.8515	0.5615
	Hb	0.0134	0.8669	0.5695
	sum	4.0012	30.0010	155.2738 (−155.2735)
methallyl dication	C_1	0.2940	5.9066	37.8009
	H	0.0042	0.7471	0.5114
	C_2	1.0922	5.7952	37.7047
	sum	1.9994	27.9976	154.1758 (154.1748)
guanidine	C	0.4996	3.9681	36.6166
	N_1	1.7924	8.4047	55.1017
	H	0.0548	0.6607	0.4928
	N_2	1.6958	8.3027	55.0697
	Ha	0.0332	0.5986	0.4637
	Hb	0.0470	0.5923	0.4595
	N_3	1.7930	8.2937	55.0724
	Ha	0.0390	0.5771	0.4524
	Hb	0.0454	0.6033	0.4650
	sum	6.0002	32.0012	204.1938 (−204.1942)
guanidinium ion	C	0.4286	3.7834	36.4879
	N	1.8224	8.3860	55.2061
	H	0.0168	0.5091	0.4148
	sum	5.9966	31.9960	204.5950 (−204.5931)

[a] *T* is the kinetic energy. Next to each sum is given the total energy obtained in the RHF calculation.

much in going to the ion, and in fact they were calculated on average to have a larger negative charge in the cation than in the parent. Most of the positive charge in the ion was borne by the hydrogens, resulting in having the charge spread over as large a volume as possible so as to reduce the electrostatic energy. As noted above, the change in the π-charges on going from guanidine to its ion was a result of the definition of "normal" π-charges. The nitrogens in both species have about the same π-electron populations.

Guanidine is considered to be an unusually strong base (pK_a 13.6), roughly comparable to hydroxide ion, and the origin of its basicity is commonly ascribed to resonance stabilization of the guanidinium ion.[2] If this resonance stabilization is not important, what is the origin of the basicity of guanidine? First, it must be recognized that hydroxyl ion in water is actually a relatively weak base. In the gas phase, hydroxyl ion will abstract a proton from toluene,[20] but no such reaction occurs in solution. The low basicity of aqueous hydroxide ion results from strong hydrogen bonding to water, stabilizing the ion. Protonation leads to the loss of the stabilization due to hydrogen bonding, and as a result the effective basicity is reduced. The basicity of guanidine probably has a similar origin. Here, it is the conjugate acid that is strongly hydrogen bonded to the solvent. As noted above, the nitrogens bear a negative charge, and the positive charge resides largely at the hydrogens that may be involved in hydrogen bonding.[21]

Conclusions

The most important conclusion that may be derived from this investigation is that 6 π-electrons do not necessarily lead to π-electron stabilization. Here we may contrast benzene with the 6-π-electron "Y-conjugated" systems. In the former, the 6 π-electrons may be distributed over 6 C–C bonds, leading to reduced electron repulsion as compared to C–C double bonds that have 2 π-electrons distributed over one C–C bond.[22] The Y dianions and guanidinium ion have 6 π-electrons distributed over three C–C or other σ-bonds, or two per bond. Therefore, there is no opportunity to reduce π-electron repulsion, and little special stabilization is found.

Experimental

Calculations. The calculations were carried out using GAUSSIAN-86[23] with standard basis sets. The integration of the charge density and the kinetic energy was carried out with PROAIMS.[24]

Acknowledgment. This investigation was supported by the National Institutes of Health. The calculations made use of a Trace computer and a Microvax GPX workstation made available via grants from the National Institute of Health.

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(21) The importance of hydrogen bonding in stabilizing guanidinium ion has been recognized, ref 19.

(22) Dewar, M. J. S.; Schmeising, H. N. *Tetrahedron* **1959**, *5*, 166; **1960**, *11*, 96.

(23) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R. A.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA 1984.

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