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Substituent Effects in the Gas Phase: 1-Substituted Allyl Anions

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Abstract: A series of 1-substituted allyl anions containing first-row, second-row, and resonance-stabilizing substituents has been examined in the gas phase with a variable-temperature flowing afterglow device. Several of these ions are weakly bound, undergo electron detachment readily, and can only be studied at subambient temperatures. The reactivity and thermodynamic properties of these species are reported. 3-Fluoropropene, 3-methoxypropene, 3-(dimethylamino)propane, and propene all have identical acidities. Electron-withdrawing and π-donating substituents (F, OCH_3, and $N(CH_3)_2$) do not destabilize allyl anion by increasing its basicity but rather by decreasing its electron-binding energy. There is, however, a linear correlation between acidity and electron affinity. Ab initio calculations reveal that the geometries of the allylic anions vary considerably as a result of a number of compensating factors, including inductive, resonance, and polarization effects. Consequently, linear free energy relationships are not applicable, and different substrates may respond to the same substituents in very different ways.

Introduction

The origin of physical organic chemistry can be traced back over 50 years to the classic work of L. P. Hammett on substituent effects and linear free energy relationships.[1] Numerous investigations of this type have been carried out and have proven to be extraordinarily fruitful.[2] More recently, extensive studies in the gas phase have provided additional insights.[3] In particular, the results are directly comparable to molecular orbital calculations and are not obscured by solvation, aggregation, or counterion effects. They can also be compared, in a meaningful way, to the myriad of data available from liquid-phase studies.[4] However, despite all the efforts that have been expended in probing gas-phase-substituent effects, little is known about the effect of different groups directly bound to a negatively charged site. This is surprising since the largest ramifications might be anticipated in this instance.

In solution, organometallic derivatives of α-heterocarbanions are of considerable synthetic importance, and a wide variety of such species have been prepared.[5] In general, second-row substituents such as SiR_3, PR_2, SR, and Cl have been found to facilitate their formation and increase their stability. The explanation for this beneficial effect has been debated, but it is now generally accepted that the increased stability is due to the large polarizability of second-row substituents and the presence of low-lying σ^* orbitals.[6] In contrast, first-row substituents such as NR_2, OR, and F are not as stabilizing as their second-row counterparts and often display conflicting effects.[7] This results from a subtle balance between diverse influences such as inductive stabilization and lone-pair lone-pair electron repulsion.

In keeping with the liquid-phase data, ab initio molecular orbital calculations on monosubstituted methyl anions (XCH_2^-) reveal the following stability order: SiH_3 (−24.9) > PH_2 (−23.0) > SH (−20.9) ≫ Cl (−13.8) > F (−9.3) > OH (−5.3) > NH_2 ≈ H (0.0) > CH_3 (+3.1) where the numbers in parentheses are stabilization energies (in kcal mol^{-1}) relative to hydrogen.[6a,8] A similar trend for first-row substituents has also been found with acyl anion derivatives ($X-CO^-$), but the magnitude of the effect is significantly larger (kcal mol^{-1}) i.e. F (−48.6) > OH (−23.6) > NH_2 (−7.9) > CH_3 (−3.7) > H (0.0).[9] The data available in the gas phase, while limited, are in accord with these calculations. Second-row α-heteroanions, a number of which have been prepared, appear to be thermodynamically more stable than their first-row counterparts.[10] Very few of the latter species, however, have actually been made, and their stabilities are somewhat varied. For example, methoxy- and fluoroacetonitrile (CH_3OCH_2CN and FCH_2CN) are more acidic than acetonitrile by only 1 and 4 kcal mol^{-1}, respectively, whereas a fluorine substituent increases the acidity of acetone by 12 kcal mol^{-1}.[11] Graul and Squires have recently generated the conjugate base of methyl fluoride and report that it is less basic than methyl anion by 7 ± 3 kcal mol^{-1}.[12] Given the disparate behavior and the limited data available, we thought it worthwhile to explore the effects of a variety of substituents on a single substrate. 1-Substituted allyl anions were chosen, in part, because the parent ion is relatively basic and large effects were anticipated. Our results from this investigation are presented herein.

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(1) Hammett, L. P. *Physical Organic Chemistry; Reaction Rates, Equilibria, and Mechanisms*; McGraw-Hill: New York, 1940.

(2) For example see: (a) Isaacs, N. S. *Physical Organic Chemistry*; John Wiley and Sons: New York, 1987. (b) March, J. *Advanced Organic Chemistry Reactions, Mechanisms, and Structure*, 3rd ed.; John Wiley and Sons: New York, 1985. (c) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; also references therein.

(3) (a) Taft, R. W. *Prog. Phys. Org. Chem.* **1987**, *16*, 1. (b) Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 247.

(4) (a) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463. (b) Taft, R. W.; Koppel, I. A.; Topsom, R. D.; Anvia, F. *J. Am. Chem. Soc.* **1990**, *112*, 2047 and references therein.

(5) (a) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277. (b) Hoppe, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 932. (c) Wierstuk, N. H. *Tetrahedron* **1983**, *39*, 205. (d) Biellmann, J. F.; Ducep, J. P. *Org. React.* **1982**, *27*, 1. (e) Krief, A. *Tetrahedron* **1980**, *36*, 2531. (f) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978. (g) Gschwend, H. W.; Rodriques, H. R. *Org. React.* **1979**, *26*, 1. (h) Peterson, D. J. *Organomet. Chem. Rev.* **1972**, *A7*, 295.

(6) (a) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467. (b) Wolfe, S.; LaJohn, L. A.; Bernardi, F.; Mangini, A.; Tonachini, G. *Tetrahedron Lett.* **1983**, *24*, 3789. (c) Lehn, J. M.; Wipff, G. *J. Am. Chem. Soc.* **1976**, *98*, 7498. (d) Epiotis, N. D.; Yates, R. L.; Bernardi, F.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 5435. (e) Streitwieser, A., Jr.; Williams, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 191.

(7) For example see: (a) Chambers, R. D.; Bryce, M. R. *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1987; Part C, Chapter 5. (b) Holtz, D. *Prog. Phys. Org. Chem.* **1971**, *8*, 32-35. (c) Streitwieser, A., Jr.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444 and references therein.

(8) Substituents with negative energies are stabilizing relative to hydrogen and those with positive values are destabilizing. See: Bernardi, F.; Mangini, A.; Tonachini, G.; Vivarelli, P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 111.

(9) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5612.

(10) (a) Ingemann, S.; Nibbering, N. M. M. *J. Chem. Soc., Perkin Trans. 2* **1985**, 837. (b) Ingemann, S.; Nibbering, N. M. M. *J. Can. J. Chem.* **1984**, *62*, 2273. (c) Tanaka, K.; MacKay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643. (d) Downard, K. M.; Sheldon, J. C.; Bowie, J. H.; Lewis, D. E.; Hayes, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8112. (e) Kass, S. R.; Guo, H. G.; Dahlke, G. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 366.

(11) All cited acidities, unless otherwise noted, come from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement 1.

(12) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517.

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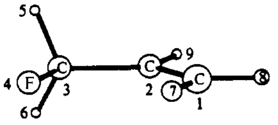
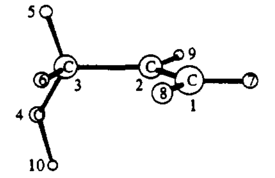
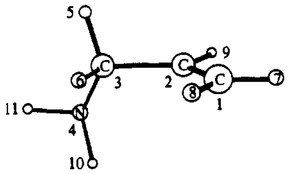
Table I. Calculated 6-31+G* Geometries of 3-Fluoro-, Hydroxy-, and Amino-Substituted Propenes[a]



C_1C_2	1.320	$C_1C_2C_3$	125.4	$C_1C_2C_3F_4$	0.0
C_2C_3	1.498	$C_2C_3F_4$	111.5	$C_1C_2C_3H_5$	119.5
C_3F_4	1.371	$C_2C_1H_7$	121.8	$C_1C_2C_3H_6$	−119.7
C_1H_7	1.074	$C_2C_1H_8$	120.9	$C_3C_2C_1H_7$	0.3
C_1H_8	1.075	$C_1C_2H_9$	120.3	$C_3C_2C_1H_8$	180.0
C_2H_9	1.079	$C_3C_2H_9$	114.3	$H_8C_1C_2H_9$	0.0
C_3H_5	1.083	$C_2C_3H_5$	110.0		
C_3H_6	1.083	$F_4C_3H_6$	107.3		



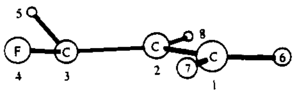
C_1C_2	1.322	$C_1C_2C_3$	124.4	$C_1C_2C_3O_4$	−125.5
C_2C_3	1.503	$C_2C_3O_4$	112.1	$C_1C_2C_3H_5$	117.6
C_3O_4	1.406	$C_2C_1H_7$	121.7	$C_1C_2C_3H_6$	−1.4
C_1H_7	1.075	$C_2C_1H_8$	121.8	$C_3C_2C_1H_7$	−179.5
C_1H_8	1.077	$C_1C_2H_9$	120.0	$C_3C_2C_1H_8$	0.0
C_2H_9	1.078	$C_3C_2H_9$	115.5	$H_8C_1C_2H_9$	−179.7
C_3H_5	1.082	$C_2C_3H_5$	110.2	$H_9C_2C_3O_4$	54.3
C_3H_6	1.087	$H_5C_3H_6$	107.8	$C_2C_3O_4H_{10}$	60.3
O_4H_{10}	0.948	$C_3O_4H_{10}$	109.9	$H_5C_3O_4H_{10}$	−179.7



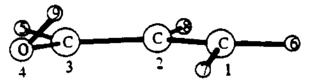
C_1C_2	1.322	$C_1C_2C_3$	124.8	$C_1C_2C_3N_4$	−126.3
C_2C_3	1.504	$C_2C_3N_4$	110.1	$C_1C_2C_3H_5$	116.3
C_3N_4	1.457	$C_2C_1H_7$	121.6	$C_1C_2C_3H_6$	−0.6
C_1H_7	1.076	$C_2C_1H_8$	121.9	$C_3C_2C_1H_7$	−179.5
C_1H_8	1.077	$C_1C_2H_9$	120.0	$C_3C_2C_1H_8$	0.3
C_2H_9	1.078	$C_3C_2H_9$	115.2	$H_8C_1C_2H_9$	−179.4
C_3H_5	1.086	$C_2C_3H_5$	109.0	$H_9C_2C_3N_4$	53.3
C_3H_6	1.090	$C_2C_3H_6$	109.5	$H_9C_2C_3H_5$	−64.1
N_4H_{10}	1.002	$N_4C_3H_5$	107.3	$C_2C_3N_4H_{10}$	66.3
N_4H_{11}	1.000	$C_3N_4H_{10}$	111.1	$C_2C_3N_4H_{11}$	−173.7
		$C_3N_4H_{11}$	111.3	$H_5C_3N_4H_{10}$	−175.2
		$H_{10}N_4H_{11}$	107.7	$H_6C_3N_4H_{10}$	−57.0

[a] All bond lengths are in angstroms and angles in degrees.

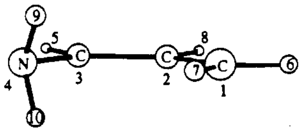
Table II. Calculated 6-31+G* Geometries of 1-Fluoro-, Hydroxy-, and Amino-Substituted Allyl Anions[a]



C_1C_2	1.376	$C_1C_2C_3$	132.4	$C_1C_2C_3F_4$	13.9
C_2C_3	1.389	$C_2C_3F_4$	115.9	$C_1C_2C_3H_5$	149.0
C_3F_4	1.409	$C_2C_1H_6$	120.5	$C_3C_2C_1H_6$	173.0
C_1H_6	1.078	$C_2C_1H_7$	121.7	$C_3C_2C_1H_7$	−2.4
C_1H_7	1.077	$C_1C_2H_8$	116.2	$H_8C_2C_1H_6$	−3.2
C_2H_8	1.085	$C_3C_2H_8$	111.3	$H_8C_2C_1H_7$	−178.6
C_3H_5	1.077	$C_2C_3H_5$	120.6	$H_8C_2C_3F_4$	−169.7
		$F_4C_3H_5$	109.0	$H_8C_2C_3H_5$	−34.7



C_1C_2	1.410	$C_1C_2C_3$	129.4	$C_1C_2C_3O_4$	2.9
C_2C_3	1.358	$C_2C_3O_4$	120.6	$C_1C_2C_3H_5$	170.3
C_3O_4	1.400	$C_2C_1H_6$	119.5	$C_3C_2C_1H_6$	175.8
C_1H_6	1.078	$C_2C_1H_7$	121.0	$C_3C_2C_1H_7$	17.5
C_1H_7	1.079	$C_1C_2H_8$	116.4	$H_8C_2C_1H_6$	−7.8
C_2H_8	1.084	$C_3C_2H_8$	114.1	$H_8C_2C_1H_7$	−166.1
C_3H_5	1.074	$C_2C_3H_5$	124.5	$H_8C_2C_3O_4$	−173.6
O_4H_9	0.952	$H_6C_1H_7$	116.1	$H_8C_2C_3H_5$	−6.2
		$O_4C_3H_5$	113.8	$C_2C_3O_4H_9$	36.3
		$C_3O_4H_9$	106.8	$H_5C_3O_4H_9$	−132.4



C_1C_2	1.398	$C_1C_2C_3$	130.5	$C_1C_2C_3N_4$	0.0
C_2C_3	1.374	$C_2C_3N_4$	122.3	$C_1C_2C_3H_5$	180.0
C_3N_4	1.444	$C_2C_1H_6$	120.6	$C_3C_2C_1H_6$	180.0
C_1H_6	1.078	$C_2C_1H_7$	122.4	$C_3C_2C_1H_7$	0.0
C_1H_7	1.078	$C_1C_2H_8$	115.2	$H_8C_2C_1H_6$	0.0
C_2H_8	1.085	$C_3C_2H_8$	114.2	$H_8C_2C_1H_7$	180.0
C_3H_5	1.076	$C_2C_3H_5$	121.7	$H_8C_2C_3N_4$	180.0
N_4H_9	1.007	$H_6C_1H_7$	117.1	$H_8C_2C_3H_5$	0.0
N_4H_{10}	1.007	$N_4C_3H_5$	116.1	$C_2C_3N_4H_9$	57.6
		$C_3N_4H_9$	110.0	$C_2C_3N_4H_{10}$	−57.7
		$C_3N_4H_{10}$	110.1	$H_5C_3N_4H_9$	−122.3
		$H_9N_4H_{10}$	105.0	$H_5C_3N_4H_{10}$	122.4

[a] All bond lengths are in angstroms and angles in degrees.

Experimental Section

All of the gas-phase experiments reported in this paper were carried out with a variable-temperature flowing afterglow apparatus which has previously been described.[13] In brief, ions are generated by electron impact and are carried down a meter long flow tube by a constant flow of a rapidly moving inert buffer gas (He in this case). Reactions are carried out in situ by adding neutral reagents at different locations along the flow tube and, thereby, converting ions from one to another. The charged products are continuously monitored with a quadrupole mass spectrometer, and the resulting real-time spectra are directly displayed on an XY recorder (manual operation) or a computer monitor (PC control).

The ability to carry out reactions at subambient temperatures was essential for the success of much of this work. Therefore, a short description of the instrumental features which pertain to temperature variability is provided.[14] The ion source and reaction region are thermally isolated by enclosing them in a vacuum box which is held at 10^{-4}–10^{-5} Torr. Resistive heaters, cooling coils, and tubing which is used for thermally pre-equilibrating the buffer gas and any selected reagent(s) are attached to a copper pipe which was split down the middle and fastened along the entire length of the flow tube. Temperatures are monitored with several type E thermocouples located along both the inside and the outside of the flow tube. A Neslab Cryocool CC-100 refrigeration system is used for temperatures down to −55 °C, and liquid nitrogen is employed to attain lower temperatures. Tubular heaters with a maximum sheath temperature of 870 °C are used to heat the apparatus. Overall, the currently accessible temperature range is ca. −190 to 400 °C.

In this work NH_2^-, OH^-, OD^-, MeO^-, t-BuO^-, and F^- were produced by electron impact on NH_3, N_2O and CH_4 (~1:2), N_2O and C_6D_{12} (~1:2), MeONO (generated in situ),[15] $(t\text{-}BuO)_2$, and NF_3, respectively. All other reactant ions were generated by fluorodesilylation or proton-transfer reactions. Allyl fluoride,[16] (*E*)- and (*Z*)-1-methoxypropene,[17] allyl methyl ether,[18] and 1-methoxy-3-(trimethylsilyl)propene[19] were prepared as previously described in the literature. Allylamine (Aldrich), allyldimethylamine (Pfaltz and Bauer), allyl chloride (Aldrich), allyl methyl sulfide (Aldrich), methyl vinyl ether (Pfaltz and Bauer), and vinyl fluoride (PCR) were obtained from the listed companies and were used as supplied. Noncondensible impurities were removed from the liquid samples via several freeze-pump-thaw cycles. Gas purities and sources

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(13) Kass, S. R.; Guo, H.; Dahlke, G. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 366.

(14) (a) Dunkin, D. B.; Fehsenfeld, F. C.; Schmeltekopf, A. L.; Ferguson, E. E. *J. Chem. Phys.* **1968**, *49*, 1365. (b) Smith, D.; Adams, N. G. *Kinetics of Ion-Molecule Reactions*; Ausloos, P., Ed.; Plenum: New York, 1979; p 345.

(15) Caldwell, G.; Bartmess, J. E. *Org. Mass Spectrom.* **1982**, *17*, 456.

(16) Puchnarevic, V. B.; Vcelak, J.; Voronkov, M. G.; Chralovsky, V. *Collect. Czech. Chem. Commun.* **1974**, *39*, 2616.

(17) Newman, M. S.; Vander Zwan, M. C. *J. Org. Chem.* **1973**, *38*, 2910.

(18) Benedict, D. R.; Bianchi, T. A.; Cate, L. A. *Synthesis* **1979**, 428.

(19) (a) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, *96*, 5560. (b) Still, W. C.; Macdonald, T. L. *J. Am. Chem. Soc.* **1974**, *96*, 5561.

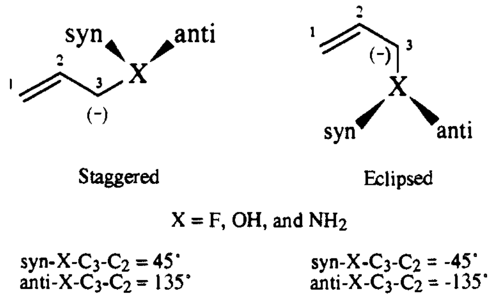
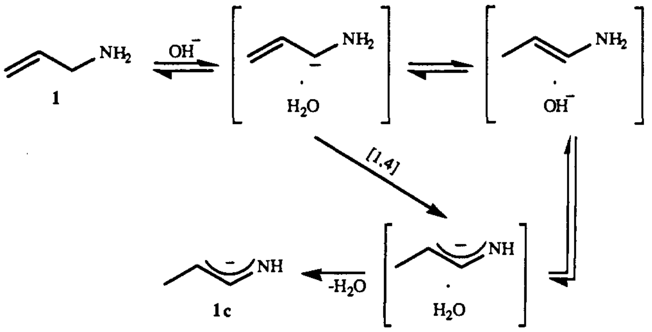


Figure 1. Initial structures for the 6-31+G* geometry optimizations of substituted propenes and allyl anions.

Scheme I



were as follows: He (Air Products, ≥99.995%), NH_3 (Linde, ≥99.999%), N_2O (Air Products, ≥99.99%), CH_4 (Air Products, ≥99.99%), NF_3 (Air Products, ≥99.0%), $(CH_3)_2NH$ (Scott, ≥99.0%), COS (Matheson, ≥97.5%), O_2 (Matheson, ≥99.6%), $^{18}O_2$ (50%, MSD), and SO_2 (Linde, ≥99.9%).

Ab initio molecular orbital calculations were carried out with Gaussian 88[20] on a Cray X-MP at the Minnesota Supercomputer Center. Structures were optimized, without imposing any symmetry constraints, at the Hartree-Fock level with the 6-31+G* basis set (Tables I and II).[21] Up to four different initial geometries were examined for each structure in an effort to obtain the lowest energy conformations. The starting points included nearly eclipsed and staggered structures as well as syn and anti rotamers for the hydroxy- and amino-substituted species (Figure 1). In the latter case, when X = OH and NH_2, the syn and anti labels represent a hydrogen and a lone pair of electrons, respectively. Vibrational frequencies for the lowest energy structures were computed with the same basis set, and each species was shown to correspond to an energy minimum, i.e. no imaginary frequencies (Table III). More reliable energies were obtained for the most stable geometries by carrying out single point calculations which include electron correlation via second-order Møller–Plesset theory (MP2/6-31+G*//6-31+G*, Table IV).[22] Tabulated acidities are given in Table V and were corrected for changes in the zero-point vibrational energies. While it is possible that some of our results do not correspond to the lowest energy conformers, given the small differences between them, it is unlikely that the acidities can be improved by even 1 kcal mol^{-1}.

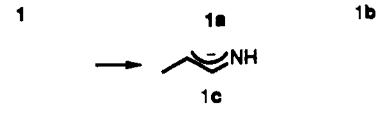
Table III. Calculated Harmonic Frequencies for a Series of Substituted Propenes, Ethylenes, and Cyclopropanes with the 6-31+G* Basis Set[a]

compd	X	frequencies, cm^{-1}
	H	210, 455, 641, 983, 1029, 1068, 1119, 1185, 1296, 1440, 1551, 1590, 1620, 1634, 1859, 3194, 3239, 3269, 3318, 3329, 3403 ($\sum$ = 37 432)
	anion	404, 459, 491, 547, 721, 1006, 1091, 1120, 1336, 1340, 1548, 1621, 1664, 3202, 3269, 3277, 3336, 3342 ($\sum$ = 29 774)
	NH_2	129, 304, 367, 484, 712, 922, 967, 1033, 1078, 1137, 1158, 1259, 1302, 1427, 1434, 1539, 1601, 1653, 1837, 1859, 3163, 3222, 3322, 3344, 3404, 3735, 3821 ($\sum$ = 46 213)
	anion	234, 272, 371, 424, 551, 677, 680, 987, 1080, 1095, 1119, 1261, 1326, 1357, 1513, 1609, 1663, 1840, 3228, 3289, 3329, 3352, 3636, 3671 ($\sum$ = 38 564)
	OH	131, 360, 372, 479, 718, 997, 1026, 1090, 1138, 1181, 1239, 1332, 1428, 1476, 1540, 1599, 1655, 1858, 3206, 3272, 3323, 3341, 3407, 4100 ($\sum$ = 40 268)
	anion	245, 328, 386, 425, 487, 630, 720, 1037, 1046, 1097, 1230, 1336, 1416, 1511, 1616, 1705, 3250, 3281, 3341, 3367, 3981 ($\sum$ = 32 435)
	F	177, 283, 615, 655, 970, 1093, 1104, 1111, 1160, 1232, 1383, 1433, 1561, 1586, 1653, 1868, 3239, 3279, 3330, 3351, 3431 ($\sum$ = 34 514)
	anion	208, 341, 450, 572, 676, 708, 965, 1086, 1104, 1238, 1364, 1466, 1594, 1693, 3241, 3295, 3322, 3369 ($\sum$ = 26 692)
	H	899, 1093, 1105, 1141, 1353, 1489, 1607, 1835, 3321, 3342, 3395, 3422 ($\sum$ = 24 002)
	anion	937, 1019, 1170, 1346, 1480, 1672, 2935, 3080, 3191 ($\sum$ = 16 830)
	NH_2	338, 499, 671, 799, 964, 1044, 1116, 1160, 1396, 1450, 1589, 1822, 1867, 3329, 3363, 3421, 3783, 3884 ($\sum$ = 32 495)
	anion	446, 526, 660, 749, 814, 1029, 1148, 1289, 1488, 1649, 1811, 3062, 3287, 3611, 3838 ($\sum$ = 25 407)
	OH	443, 530, 777, 972, 1044, 1119, 1226, 1432, 1460, 1589, 1853, 3332, 3409, 3433, 4092 ($\sum$ = 26 711)
	anion	491, 529, 768, 804, 937, 1154, 1313, 1493, 1673, 3177, 3303, 4188 ($\sum$ = 19 830)
	F	523, 792, 1025, 1037, 1080, 1272, 1451, 1551, 1870, 3359, 3432, 3454 ($\sum$ = 20 846)
	anion	536, 791, 800, 833, 1139, 1446, 1685, 3228, 3319 ($\sum$ = 13 777)
	H	806, 806, 922, 951, 951, 1180, 1180, 1223, 1261, 1296, 1326, 1326, 1610, 1610, 1673, 3303, 3303, 3317, 3377, 3377, 3400 ($\sum$ = 38 198)
	anion	796, 808, 858, 908, 972, 1120, 1132, 1209, 1236, 1285, 1313, 1610, 1635, 3040, 3137, 3159, 3195, 3211 ($\sum$ = 30 624)
	NH_2	305, 430, 439, 834, 874, 915, 942, 986, 1086, 1177, 1205, 1250, 1286, 1312, 1338, 1386, 1547, 1598, 1660, 1837, 3267, 3306, 3316, 3388, 3402, 3733, 3817 ($\sum$ = 46 636)
	anion	187, 431, 435, 770, 823, 878, 967, 971, 1088, 1114, 1128, 1207, 1268, 1282, 1314, 1585, 1615, 1815, 3191, 3199, 3240, 3258, 3672, 3741 ($\sum$ = 39 179)
	OH	345, 437, 444, 821, 884, 907, 1023, 1075, 1174, 1200, 1247, 1292, 1308, 1341, 1412, 1546, 1596, 1661, 3305, 3312, 3323, 3386, 3404, 4097 ($\sum$ = 40 540)
	anion	124, 422, 441, 760, 813, 860, 954, 976, 1114, 1116, 1159, 1223, 1280, 1352, 1583, 1615, 3198, 3207, 3246, 3267, 4192 ($\sum$ = 32 902)
	F	426, 439, 806, 881, 892, 1058, 1077, 1180, 1203, 1248, 1296, 1304, 1335, 1524, 1594, 1659, 3313, 3320, 3387, 3395, 3411 ($\sum$ = 34 748)
	anion	424, 430, 700, 817, 820, 941, 972, 1109, 1113, 1179, 1251, 1285, 1581, 1615, 3222, 3232, 3280, 3299 ($\sum$ = 27 270)

[a] No scaling factor has been applied.

Results

Allylamine (1). Strong bases such as NH_2^-, OH^-, and CH_3O^- react readily with allylamine to afford an *m/z* 56 ion (M − 1).[23] This species is protonated by the Bronsted acids CH_3CN, $(CH_3)_3COH$, and CH_3CH_2OH (slow reaction) but not by H_2O or CH_3OH. These results, in conjunction with hydrogen–deuterium exchange experiments, bracket the proton affinity of the M − 1 ion (PA = 376 ± 3 kcal mol^{-1}). The basicity, however, is not in accord with expectation for **1a** or **1b**, both of which could result from simple deprotonation of **1** (eq 1). In addition, the M − 1 ion undergoes 2 H/D exchanges upon reaction with D_2O, CH_3OD,



(1a)

(1b)

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(20) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1988.

(21) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Spitznegel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363. (c) Clark, T.; Chandrasekhar, J.; Spitznegel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(22) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

(23) The reference compounds used in bracketing experiments are listed in Table VI, and their acidities come from ref 11.

Table IV. Calculated Energies (in hartrees) for a Series of Substituted Propenes, Ethylenes, and Cyclopropanes

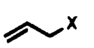
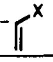
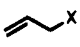
substituent	basis set						
H	6-31+G*	−117.075442	−116.425201	−78.035817	−77.363926	−117.060917	−116.372790
	MP2	−117.462084	−116.826908	−78.290489	−77.628380	−117.454674	−116.781352
NH_2	6-31+G*	−172.098079	−171.451890	−133.068835	−132.406698	−172.087817	−171.401304
	MP2	−172.649679	−172.022844	−133.489908	−132.840251	−172.647414	−171.981256
OH	6-31+G*	−191.926422	−191.277954	−152.895625	−152.242684	−191.913579	−191.237750
	MP2	−192.492293	−191.865602	−153.331191	−152.691690	−192.487182	−191.831030
F	6-31+G*	−215.928779	−215.281769	−176.891365	−176.251567	−215.914456	−215.251442
	MP2	−216.485962	−215.859344	−177.319142	−176.692104	−216.479252	−215.834473

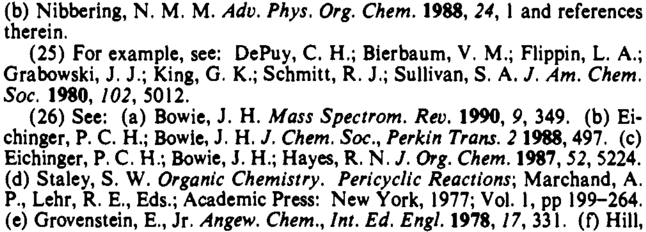
Table V. Calculated and Experimental Acidities for Substituted Propenes, Ethylenes, and Cyclopropanes[a]

	acidity[b]		
substituent X			
H	388.7 (390.8)[c]	406.3 (409.4)[d]	412.8 (412)[c]
NH_2	383.2 (390 ± 4)	398.5	408.4
OH	383.2 (390 ± 4)	392.4 (397 ± 3)[e]	401.8
F	383.5 (390 ± 4)	384.4 (387 ± 3)[f]	395.0

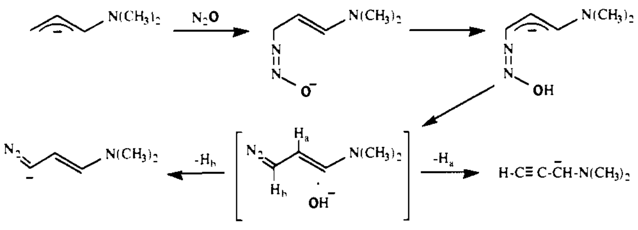
[a] All values are in kcal mol^{-1} and correspond to the acidic site bearing the X substituent. [b] MP2/6-31+G*//6-31+G* with zero-point vibrational energy corrections (frequencies were scaled by a factor of 0.9). Experimental values are in brackets. [c] See ref 11. [d] See: Ervin, K. M. et al. *J. Am. Chem. Soc.* **1990**, *112*, 5750. [e] This value is for the methyl ether, which was bracketed and found to lie between $(CH3)_2$-NH and $EtNH_2$. [f] Unpublished data, J. Rabasco.

and EtOD (some EtO^- is also formed), whereas **1a** and **1b** would be expected to undergo 3 and 1 exchanges, respectively.[24] Therefore, an alternative structure, 3-methyl-1-azaallyl anion (**1c**), is proposed, and two reasonable pathways for its formation are given in Scheme I. In one of the mechanisms isomerization occurs via a series of proton-transfer reactions and in the other it takes place by a 1,4-proton shift. The two pathways can be distinguished by reacting **1** with OD^-, and our results are consistent with the former process; d_0 (*m/z* 56) and d_1 (*m/z* 57) M − 1 ions are formed in approximately equal amounts. This result is not surprising since multiple proton-transfer mechanisms are well precedented[24,25] but 1,4-rearrangements, be it in the gas phase or in condensed media, are not.[26]

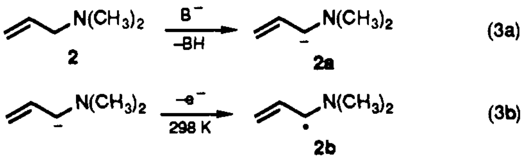
The reactivity of **1c** with a variety of standard reagents (N_2O, O_2, SO_2, and CS_2) has been examined, and the reaction products, which are consistent with previously reported mechanistic pathways, are summarized in eqs 2a–d.[27,28]



Scheme II



Allyldimethylamine (**2**). To prepare a 1-amino-substituted allyl anion, and prevent any rearrangement upon deprotonation, allyldimethylamine was examined. Several bases, including OH^- and NH_2^-, react readily with **2**, but no new ionic products are detected, i.e. the reactant ion signal disappears and nothing replaces it. A plausible explanation for this behavior is that the conjugate base is formed but it is thermally labile and readily decomposes (eq 3). In other words, the formation of **2a** is accompanied by facile electron detachment. Given that allyl anion binds its electron by only 0.357 eV (8.2 kcal mol^{-1}),[29] a perturbation of 2 or 3 kcal mol^{-1} could account for this behavior in the multicollision environment of a flowing afterglow (FA) apparatus. However, it should be added that this problem is not unique to the FA, and weakly bound anions are also a challenge to prepare in the lower pressure regimes of an ion cyclotron resonance spectrometer.[28a] In any case, this hypothesis suggests that deprotonation at lower temperatures, where electron detachment is less likely to take place, might lead to the observation of **2a**. And, indeed, when our variable-temperature flowing afterglow is cooled down to ca. −55 °C, a temperature easily attained in this apparatus, a strong M − 1 ion (**2a**, *m/z* 84) is observed upon reaction of strong bases with allyldimethylamine.



The acidity of **2** was bracketed by carrying out a series of reactions with bases of different strength. Amide and hydroxide deprotonate allyldimethylamine, but methoxide and the conjugate base of furan do not. The reverse direction, protonating **2a**, was also examined to ascertain the importance of any kinetic effects. However, since protonation can occur at both ends of the allylic system the results from the two sets of experiments can, in principle, differ by several kilocalories per mole.[30] In any case, ND_3 and $(CH_3)_2NH$ do not react with the M − 1 ion (except for a little clustering), whereas it is protonated by stronger acids such as furan and D_2O. In the latter case, a trace of hydrogen–deuterium exchange is also observed. Consequently, we assign

---

(24) For a discussion on H/D exchange see: (a) Grabowski, J. J.; DePuy, C. H.; Van Doren, J. V.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384. (b) Nibbering, N. M. M. *Adv. Phys. Org. Chem.* **1988**, *24*, 1 and references therein.

(25) For example, see: DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

(26) See: (a) Bowie, J. H. *Mass Spectrom. Rev.* **1990**, *9*, 349. (b) Eichinger, P. C. H.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1988**, 497. (c) Eichinger, P. C. H.; Bowie, J. H.; Hayes, R. N. *J. Org. Chem.* **1987**, *52*, 5224. (d) Staley, S. W. *Organic Chemistry. Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, pp 199–264. (e) Grovenstein, E., Jr. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 331. (f) Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123 and references therein.

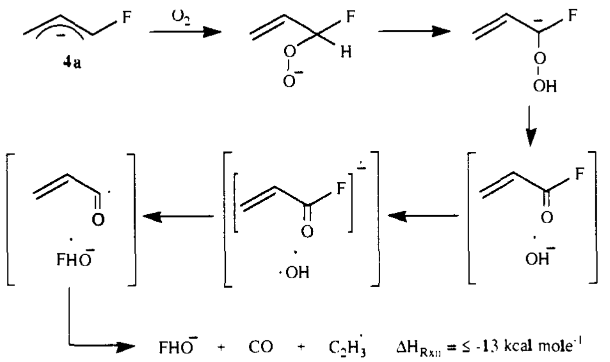
(27) Minor products (≤5%), unless otherwise noted, are not reported in this paper.

(28) (a) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849. (b) Schmitt, R. J.; Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 6443. (c) Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H. *Environ. Health Perspect.* **1980**, *36*, 119. (d) DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556.

(29) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734.

(30) The difference between the acidity of a 3-substituted propene and the proton affinity of its conjugate base is equal to the difference in the heats of formation of the 1- and 3-substituted olefins. On the basis of available thermochemical data, it appears that this disparity is less than 4 kcal mol^{-1} for the compounds of interest, i.e. **2**, **3**, and **4**. It is not surprising, therefore, that the bracketed acidities and PA's appear to be the same. Given this complication the uncertainties in the acidities are estimated somewhat conservatively.

Scheme III



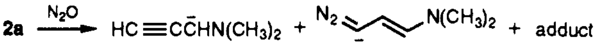
$\Delta H_{\mathrm{acid}}(\mathbf{2})$ = 390 ± 4 kcal mol^{-1}.

The 1-(dimethylamino)allyl radical (**2b**) must have a positive electron affinity because the corresponding anion is an observable species. It is likely to be less than 0.357 eV (8.2 kcal mol^{-1}),[29] because **2a**, unlike allyl anion, cannot readily be observed in a FA at room temperature. Therefore, we assign EA (**2b**) = 4 ± 4 kcal mol^{-1}. This value is reproduced by substituting our acidity for **2** and its allylic C–H bond dissociation energy (BDE, 80 kcal mol^{-1})[31] into eq 4. The electron affinity is also consistent with

$$\mathrm{BDE}(\mathbf{2}) = \Delta H_{\mathrm{acid}}(\mathbf{2}) - \mathrm{IP}(\mathrm{H}^{\bullet}) + \mathrm{EA}(\mathbf{2b}) \qquad (4)$$

the observation that **2a** undergoes electron transfer to SO_2 (EA = 1.11 eV), CS_2 (EA = 0.6 eV, some adduct is also observed), and O_2 (EA = 0.45 eV, the enolates of ketene and acetaldehyde are formed as well).[32]

The reactivity of **2a** is, in general, dominated by its tendency to undergo electron transfer and clustering reactions. The latter are a consequence of the low temperatures which are required to generate the anion. Nitrous oxide, however, does react in a characteristic manner to afford a diazo anion (*m/z* 110), a dehydrogenated product (*m/z* 82), and an adduct (*m/z* 128, eq 5).[33] A plausible mechanism is illustrated in Scheme II and really is no different than a previously proposed pathway.[28a]

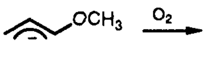


m/z	82	110	128
	~1	6	10

(5)

Allyl Methyl Ether (3). At room temperature in our flowing afterglow apparatus we are unable to prepare more than a trace of 1-methoxyallyl anion (**3a**) from allyl methyl ether or a mixture of (*E*)- and (*Z*)-1-methoxypropene. Deprotonation with OH$^-$ or NH_2^- leads to virtually a complete loss of signal; only minuscule amounts of methoxide, allyloxide ($CH_2{=}CHCH_2O^-$), and the M − 1 ion are observed. At subambient temperatures, acid–base chemistry and fluorodesilylation of 1-methoxy-3-(trimethylsilyl)propene give rise to substantial amounts of **3a**. Allyl methyl ether, however, was found to be a better source of the M − 1 ion than the mixture of (*E*)- and (*Z*)-1-methoxypropene.

The acidity of allyl methyl ether was measured with use of the bracketing technique. Strong bases such as amide and hydroxide deprotonate **3**, but methoxide and the conjugate base of furan do not. Conversely, NH_3 and $(CH_3)_2NH$ do not protonate **3a**, whereas CH_3OD, furan, and D_2O do. Hydrogen–deuterium exchange is not particularly revealing in that it does not take place with ND_3, $EtND_2$, *i*-$PrND_2$, D_2O, or CH_3OD at ca. −55 °C. Nevertheless, on the basis of the above data $\Delta H_{\mathrm{acid}}(\mathbf{3})$ = 390 ± 4 kcal mol^{-1} is assigned, and an electron affinity of 5 ± 4 kcal mol^{-1} (0.22 ± 0.17 eV) for the corresponding radical is derived via eq 4. The latter quantity is in accord with the observation that **3a** undergoes electron transfer to SO_2, CS_2 (a large amount of adduct and a minor amount of adduct $-CH_3OH$ are also formed), and O_2 (a number of additional products are observed, eq 6).



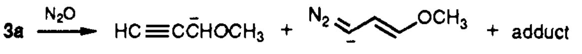
3a

$$HC{\equiv}C^- + CH_3O^- + O_2^- + HC{\equiv}CO^- + CH_2CHO^- + CH_2{=}\bar{C}CHO$$

m/z	25	31	32	41	43	55
	~1	1	2	6	1	1

(6)

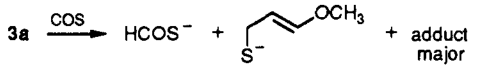
The reactivity of **3a** with N_2O, CO_2, and COS has been explored (eqs 7–9). Nitrous oxide reacts in an analogous fashion to **2a** to afford a characteristic diazo anion as the major product. Hydride transfer and addition products are observed in the reactions with CO_2 and COS, and in the latter case some sulfur atom transfer also takes place. These results are consistent with an estimated hydride binding energy for **3a** of 50 kcal mol^{-1}.[34]



~2 12 3

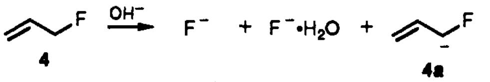
(7)

$$\mathbf{3a} \xrightarrow{CO_2} HCO_2^- + \underset{\text{major}}{\text{adduct}} \qquad (8)$$



(9)

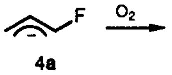
Allyl Fluoride (4). Given the behavior of allyl methyl ether and allyldimethylamine, it was somewhat surprising to find that allyl fluoride reacts with strong bases (OH$^-$ and NH_2^- but not CH_3O^- or the conjugate bases of furan and fluorobenzene) at room temperature to afford an abundant M − 1 ion (*m/z* 59, eq 10).



~20% 15% 65%

(10)

This anion deprotonates methanol, furan, and fluorobenzene which leads us to assign $\Delta H_{\mathrm{acid}}(\mathbf{4})$ = 390 ± 4 kcal mol^{-1}. Substitution of this value along with the allylic C–H bond dissociation energy (88.6 kcal mol^{-1})[31] into eq 4 affords an electron affinity for the corresponding radical of 13 ± 5 kcal mol^{-1} (0.56 ± 0.17 eV). This result is consistent with our ability to form **4a** at 20 °C and the fact that it undergoes electron transfer to SO_2 and O_2. In the latter reaction (eq 11) a number of products are formed, most



4a

$$F^- + HC{\equiv}C^- + O_2^- + OHF^- + HC{\equiv}CO^- + CH_2{=}CHCO_2^- \qquad (11)$$

m/z	19	25	32	36	41	71
	~3	1	1	1	1	1

of which can be accounted for by pathways that have previously been reported.[28b,c] One species worth commenting on, however, is the ion at *m/z* 36. This product almost assuredly is OHF$^-$ given the unusual mass and the lack of other reasonable possibilities. Additional support for this assignment, and the others in eq 11, was obtained by using labeled $^{18}O_2$. In particular, the ion at *m/z*

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[31] All of the bond dissociation energies either were estimated using one of the following schemes, BDE($HOCH_2$–H) − BDE($CH_2{=}CH$–C(OH)H–H) = BDE(XCH_2–H) − BDE($CH_2{=}CH$–CXH–H) and BDE($CH_2{=}CH$–CH_2–H) − BDE($PhCH_2$–H) = BDE($CH_2{=}CH$–C(C_2H_5)H–H) − BDE-(PhC(C_2H_5)H–H), or were obtained from the following sources: (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (b) *Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, FL, 1989–1990. (c) Alfassi, Z. B.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1973**, *5*, 155.

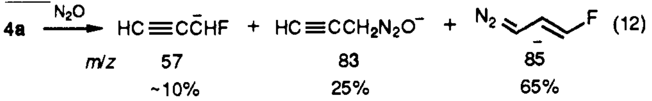
[32] References for the EA's are as follows: (SO_2) (a) Celotta, R. J.; Bennett, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740. (b) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574. (CS_2) (c) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 45. (O_2) (d) Travers, M. J.; Cowles, D. C.; Ellison, G. B. *Chem. Phys. Lett.* **1989**, *164*, 449.

[33] Addition of N_2O to the internal end of the allylic system could lead to a different isomer of the *m/z* 82 ion.

[34] The hydride ion binding energy was derived with use of $\Delta H_f(\mathbf{3a})$ = −9.3, ΔH_f(methoxyallene) = 5.5, and $\Delta H_f(\mathrm{H}^-)$ = 34.7, where all of the thermodynamic data come from ref 11 and: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976.

36 shifts to *m/z* 38 upon reaction with isotopically labeled oxygen. A reasonable mechanism for the formation of this unusual species is given in Scheme III.

The reactivity of 1-fluoroallyl anion was explored with a series of reagents, including N_2O, COS, and CS_2 (eqs 12–14). Nitrous oxide reacts to produce the expected diazo anion (*m/z* 85) and dehydrogenation product (*m/z* 57), but it also affords an ion that corresponds to addition followed by loss of hydrogen fluoride (*m/z* 83). Similar products, adduct–HF, are observed in the reactions with COS and CS_2, although in the former case sulfur atom transfer also occurs. The dominant pathway, however, with the latter two reagents appears to be loss of an electron, i.e. disappearance of the signal.

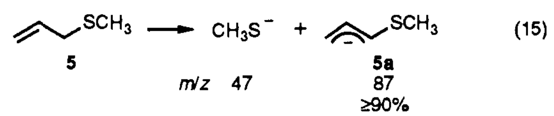


(12)

$$\mathbf{4a} \xrightarrow{\text{COS}} \underset{\sim 3}{{}^-SCH_2CH{=}CHF} + \underset{6}{HC{\equiv}CCH_2COS^-} + \underset{1}{{}^-SCH_2C{\equiv}CH} + \underset{1}{\text{adduct}} + \text{signal loss} \qquad (13)$$

$$\mathbf{4a} \xrightarrow{CS_2} \underset{\sim 1}{HC{\equiv}CCH_2CS_2^-} + \underset{2}{\text{adduct}} + \text{signal loss} \qquad (14)$$

Allyl Methyl Sulfide (5), A wide variety of bases (OH^-, MeO^-, EtO^-, *i*-PrO^-, *t*-BuO^-, but not CH_2CN^- and F^-) react with allyl methyl sulfide to afford an M − 1 ion (*m/z* 87) along with minor amounts of methanethiolate (*m/z* 47, eq 15). The M − 1 ion



(15)

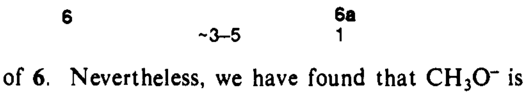
readily exchanges 3 hydrogens for deuterium upon interaction with CH_3OD and EtOD as expected for a 1-substituted allyl anion. Deuterium oxide and *t*-BuOD also lead to H–D exchange but the process is very inefficient, and in the latter case it is dominated by deuteron transfer. On the basis of these data, and the fact that CH_3CN and *i*-PrOH both protonate the M − 1 ion, we assign $\Delta H_{acid}(\mathbf{5}) = 375 \pm 3$ kcal mol^{-1}. Application of this value via eq 4 leads to an electron binding energy for **5a** of 23 ± 5 kcal mol^{-1} (1.00 ± 0.22 eV) when an allylic C–H bond dissociation energy of 84 kcal mol^{-1} is used.[31]

The reactivity of **5a** was explored, but given its relative stability it was not surprising that it is not very reactive. Nitrous oxide is inert to the M − 1 ion, and adducts are formed upon reaction with CS_2 and SO_2. In the latter case, this is only a minor product (~10%) and electron transfer, which is consistent with the assigned EA, predominates. The M − 1 ion also undergoes a very slow but potentially interesting reaction with O_2 (eq 16).

$$\mathbf{5a} \xrightarrow{O_2} \underset{\substack{17\\ \sim 5}}{OH^-} + \underset{\substack{33\\ 1}}{HO_2^-} + \underset{\substack{47\\ 6}}{CH_3S^-} + \underset{\substack{61\\ 2}}{HCSO^-} + \underset{\substack{71\\ 1}}{CH_2{=}\bar{C}CHO} + \underset{\substack{74\\ 1}}{C_3H_6S^-} \qquad (16)$$

m/z 17, 33, 47, 61, 71, 74

Allyl Chloride (6), The conjugate base of allyl chloride (**6a**) can be prepared in useful quantities by deprotonation with OH^- and NH_2^-, but it is difficult to generate and the major product is chloride (eq 17). The resulting anion reacts readily with many Bronsted acids to afford Cl^-, and this makes it difficult to bracket the acidity of **6**. Nevertheless, we have found that CH_3O^- is capable of generating a small amount of the M − 1 ion (in addition to chloride), whereas EtO^-, *i*-PrO^-, *t*-BuO^-, F^-, and CH_2CN^- only lead to the formation of Cl^-. On the other hand, D_2O induces some H/D exchange along with the formation of Cl^-, CH_3OD reacts to afford Cl^- exclusively, EtOD yields a trace of ethoxide in addition to Cl^-, and stronger acids such as *i*-PrOH and *t*-BuOH readily undergo proton transfer. On the basis of these results, our best estimate for $\Delta H_{acid}(\mathbf{6})$ is 379 ± 4 kcal mol^{-1}. Substitution of this value and the allylic C–H BDE (88.6 kcal mol^{-1})[31] into eq 4 leads to an EA for the corresponding radical of 24 ± 5 kcal mol^{-1} (1.04 ± 0.22 eV). This latter assignment is consistent with the observation that electron transfer occurs from **6a** to SO_2.



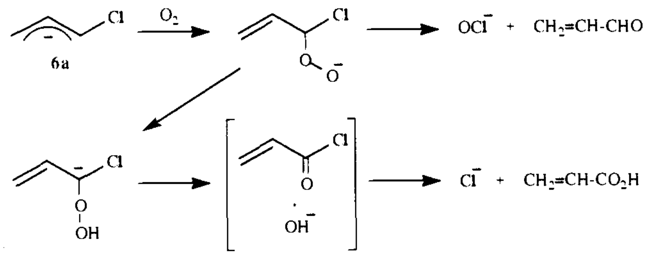
(17)

Table VI. Acidities of Reference Acids Used in Bracketing Experiments[a]

acid	ΔH_{acid}	acid	ΔH_{acid}
NH_3	403.7	CH_3OH	380.6
$(CH_3)_2NH$	396.2	EtOH	377.4
D_2O	392.0	*i*-PrOH	375.4
H_2O	390.8	*t*-BuOH	374.6
furan	388	CH_3CN	372.9
fluorobenzene	387.2	HF	371.3
CH_3OD	382.5		

[a] All values come from ref 11 and are in kcal mol^{-1}.

Scheme IV



1-Chloroallyl anion (**6a**) does not react with N_2O and affords chloride upon reaction with CS_2 and O_2 (eqs 18 and 19). A small

$$\mathbf{6a} \xrightarrow{CS_2} \underset{\sim 7-8}{Cl^-} + \underset{1}{HC{\equiv}CCH_2CS_2^-} \qquad (18)$$

$$\mathbf{6a} \xrightarrow{O_2} \underset{\sim 3}{Cl^-} + \underset{1}{OCl^-} \qquad (19)$$

amount of a product corresponding to adduct–HCl (*m/z* 115) is also observed in the former case, and a little hypochlorite (*m/z* 51 and 53) is generated in the latter reaction. Mechanistically, carbon disulfide is known to react via addition/fragmentation pathways, but the formation of OCl^-, which presumably involves nucleophilic attack on chlorine, is unusual. A reasonable pathway for it is given in Scheme IV.

Discussion

A series of 1-substituted allyl anions with first-row (CH_3, $N(CH_3)_2$, OCH_3, and F), second-row (SCH_3 and Cl), and resonance-stabilizing (CN, CHO, C_6H_5, and C_2H_3) substituents have been examined. The electron affinities of the first-row species are relatively small, and two of them, **2a** and **3a**, are difficult to prepare because they undergo facile electron detachment. In our variable-temperature flowing afterglow device this decomposition pathway can be suppressed by synthesizing these ions at subambient temperatures. As a result, 1-dimethylamino and 1-methoxyallyl anions (**2a** and **3a**, respectively) are readily generated below ca. −20 °C. These methyl derivatives of the parent compounds were used for our studies because deprotonation of allylamine (**1**) does not afford the desired 1-aminoallyl anion. A rearrangement takes place instead, and 3-methyl-1-azaallyl ion (**1c**) is formed (Scheme I). This result serves as a useful reminder that proton-transfer reactions are not always "simple" and that great care must be exercised before assigning ion structures.

Allyl anions with first-row substituents are more basic than the corresponding second-row and resonance-stabilizing derivatives (Table VII). This observation is not surprising and is consistent with previous reports.[10] It is startling, however, that 3-dimethylamino-, methoxy-, and fluoropropene (**2**, **3**, and **4**, respectively) all have the same acidity and, within experimental

Table VII. Acidities, Bond Dissociation Energies, and Electron Affinities for a Series of Substituted Propenes[a]

 X =	ΔH_{acid}	BDE[b]	EA
H	390.8[c]	86.3	8.2
$N(CH_3)_2$	390 ± 4	80	4
OCH_3	390 ± 4	81	5
F	390 ± 4	88.6	13
SCH_3	375 ± 3	84	23
Cl	379 ± 4	88.6	24
CH_3	386 ± 5[d]	82.5	10
CHO	355.0[c]	83	42
C_6H_5	368 ± 4[e]	78	24
CN	360 ± 4[e]	81	35
C_2H_3	368.6[c]	76	21

[a] All values in kcal mol^{-1}. [b] See ref 31 for all the bond dissociation energies. [c] Reference 11. [d] The acidity of 1-butene is between that of H_2O and CH_3OH. [e] 3-Phenylpropene and 3-cyanopropene (both are available from Aldrich) were bracketed (unpublished data, P. Chou), and the relevant data are as follows: Pyrrole (ΔH_{acid} = 358.7 kcal mol^{-1}), trifluoroethanol (ΔH_{acid} = 361.8 kcal mol^{-1}), acetaldehyde (ΔH_{acid} = 365.8 kcal mol^{-1}), and acetone oxime (ΔH_{acid} = 366.1 kcal mol^{-1}) protonate the conjugate base of 3-phenylpropene, whereas diethylhydroxylamine (ΔH_{acid} = 370.6 kcal mol^{-1}) does not. In the reverse direction, fluoride and stronger bases deprotonate the olefin and thus we assign ΔH_{acid} = 368 ± 4 kcal mol^{-1}. In the case of 3-cyanopropene, 2-methyl-2-propanethiol (ΔH_{acid} = 352.5 kcal mol^{-1}), methanethiol (ΔH_{acid} = 356.9 kcal mol^{-1}), and formamide (ΔH_{acid} = 359.9 kcal mol^{-1}) protonate the conjugate base but acetaldehyde does not. Conversely, the conjugate bases of acetaldehyde and formamide deprotonate 3-cyanopropene leading to ΔH_{acid} = 360 ± 4 kcal mol^{-1}.

uncertainty, it is the same as that of propene. In other words, replacing a methyl hydrogen in propene by F, OCH_3, or $N(CH_3)_2$ leads to no change in the acidity. Since the electronegativities (F > OCH_3 > $N(CH_3)_2$) and π-donating abilities ($N(CH_3)_2$ > OCH_3 > F) of these substituents are very different, an acidity ordering such as F > OCH_3 > $N(CH_3)_2$ ≈ H might have been expected. The contrast between the observed and anticipated results suggests that a delicate balance exists between a variety of variables, including electronegativity, resonance, polarization, and the field effect. The observed acidity ordering does account for the greater electron binding energy of fluoroallyl anion compared to **2a** and **3a**; the C–H BDE's in the conjugate acids presumably differ as in CH_3X, i.e. FCH_2–H > CH_3OCH_2–H ≈ $(CH_3)_2NCH_2$–H,[31] and thus the electron affinities are dictated by thermodynamic considerations as given in eq 4.

Linear free energy relationships with Taft's σ_X, σ_F, σ_R, and σ_α parameters have been explored to try and explain the observed acidities of 3-substituted propenes.[3] No satisfactory correlation was obtained, which is in contrast to the work of Bartmess and Burnham on 2-substituted derivatives.[35] This failure is not surprising since the substituents are located directly at the charged site and provide too large a perturbation on the system. We have found, on the other hand, that there is a linear relationship between acidity and electron affinity (Figure 2). This empirical correlation indicates that the dominant effect of a substituent on a 1-substituted allyl anion is on the stability of the anion and *not* the corresponding radical.

To obtain further insights, ab initio molecular orbital calculations have been carried out on several propenes and their conjugate bases. Geometry optimizations were performed with gradient techniques and without imposing any symmetry constraints. The 6-31+G* basis set, which includes diffuse orbitals and polarization functions, both of which are needed to accurately describe negative ions, was used (Tables I and II).[21,36] Harmonic frequencies were computed for each structure to ensure that they correspond to minima on the potential energy surface and to provide zero-point vibrational energies (Table III). Improved energies were also obtained by accounting for electron correlation with second-order Møller–Plesset theory (Table IV).[22] The resulting deprotonation energies (DPE's, Table V) are directly comparable to the experimental results with one caveat—we have modeled the methoxy and dimethylamino groups by OH and NH_2 to facilitate the calculations. This type of substitution has previously been carried out and should only be of minor consequence.[6a] In accord with this view, the relative acidities are found to be in excellent agreement with experiment. The absolute values, however, are not nearly as good and are approximately 5 kcal mol^{-1} too low. This discrepancy does not result from temperature differences (0 K vs 218 or 298 K), which only lead to changes of ~0.5 kcal mol^{-1}. It therefore appears that more elaborate calculations are needed to obtain better deprotonation energies. A few such computations have been carried out, fourth-order Møller–Plesset theory (MP4(SDTQ)/6-31+G*//6-31+G*) and MP2 calculations with a bigger basis set (MP2/6-311++G**//6-31+G*), and they do lead to a modest improvement (1.7 and 2.2 kcal mol^{-1}, respectively) in the DPE of 3-fluoropropene.

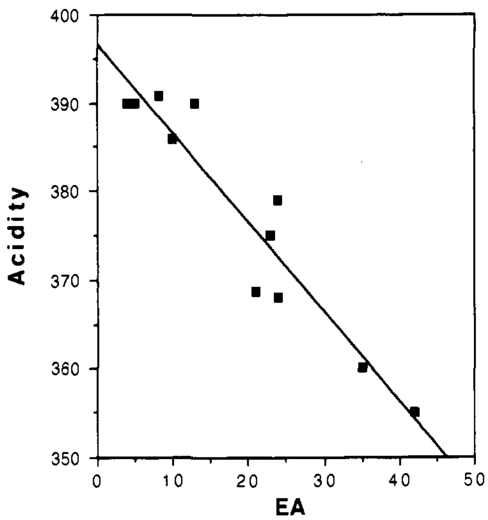


Figure 2. Experimental acidities vs electron affinities for a series of 3-substituted propenes. The solid line is from a least-squares fit of the data: $y = -1.01 + 397$; $r = 0.95$.

The calculated geometries of 3-fluoropropene (**4**), 3-hydroxypropene (**7**), and 3-aminopropene (**1**, Table I) are reasonable and in accord with experimental data,[37] but are not particularly revealing. In contrast, considerable insight can be obtained by examining the structures of the conjugate bases (**4a**, **7a**, and **1a**). Both **4a** and **7a** are calculated to be nonplanar and are not delocalized to the maximum extent.[38] This results in a loss of energy which must be balanced by a reduction in electron–electron repulsion between the π-system and the lone-pair electrons. The two ions, nevertheless, are structurally quite distinct. 1-Fluoroallyl anion is pyramidal at C3 (F4 is 13.9° and H5 is 31° out of the C1–C2–C3 plane) and somewhat flatter at C1 (H6C1C2C3 =

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(35) Bartmess, J. E.; Burnham, R. D. *J. Org. Chem.* **1984**, *49*, 1382.

(36) (a) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986. (c) Nobes, R. H.; Poppinger, D.; Li, W.-K.; Radom, L. *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1987; Part C, Chapter 1.

(37) 3-Fluoropropene: (a) Durig, J. R.; Zhen, M.; Heusel, H. L.; Joseph, P. J.; Groner, P.; Little, T. S. *J. Phys. Chem.* **1985**, *89*, 2877. (b) Durig, J. R.; Zhen, M.; Little, T. S. *J. Phys. Chem.* **1984**, *81*, 4259. Allyl alcohol: (c) Badawi, H.; Lorencak, P.; Hillig, K. W., II; Imachi, M.; Huczkowski, R. L. *J. Mol. Struct.* **1987**, *162*, 247. (d) Vanhouteghem, F.; Pyckhout, W.; Van Alsenoy, C.; Van Den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1986**, *140*, 33. Allylamine: (e) Wiedenmann, K. H.; Botskor, I.; Rudolph, H. D. *J. Mol. Struct.* **1988**, *190*, 173. (f) Yamanouchi, K.; Matsuzawa, T.; Kuchitsu, K.; Hamada, Y.; Tsuboi, M. *J. Mol. Struct.* **1985**, *126*, 305. (g) Durig, J. R.; Sullivan, J. F.; Whang, C. M. *Spectrochim. Acta* **1985**, *41A*, 129.

(38) Ab initio calculations with the 3-21+G basis set have recently been carried out on **4a**, and the results are very similar to those reported here. Tonachini, G.; Canepa, C. *Tetrahedron* **1989**, *45*, 5163. The conjugate base of *P*-allylphosphonic diamide, a 1-heterosubstituted allyl anion, has also been the subject of study. It is calculated to be planar, but the corresponding lithiated species is found to be pyramidal at C1 or C3 depending upon the conformation (*E* or *Z*). Denmark, S. E.; Cramer, C. J. *J. Org. Chem.* **1990**, *55*, 1806.

7° and H7C1C2C3 = 2.4°). As a result the charge tends to localize at C3, which is consistent with the Mulliken population analysis and the fact that C2–C3 is longer than C1–C2 by 0.013 Å. The structure is also in accord with the electronegativity of fluorine, its preference for bonding at sp^3 centers, and its relatively poor π-donating abilities. The geometry of 1-hydroxyallyl anion (**7a**), on the other hand, reflects the fact that oxygen is not as electronegative as fluorine and is a better π-electron donor. The negative charge is shifted away from the substituent leading to a flattening out at C3 (O4C3C2C1 = 2.9° and H5C3C2C1 = 9.7°), increased pyramidalization at C1 (H7C1C2C3 = 17.5° and H6C1C2C3 = 4.2°), and a large difference in bond lengths (0.052 Å) between C1–C2 (long) and C2–C3 (short). 1-Aminoallyl anion (**1a**), in stark contrast to **4a** and **7a**, is calculated to be planar, and the geometry is quite similar to that of the parent ion.[39] Nitrogen only has one lone-pair of electrons and it is orthogonal to the π-system. This eliminates the driving force for distorting the carbon framework and means that the strong π-donating ability of an amino group is not destabilizing in this instance. The greater delocalization in **1a**, relative to **4a** and **7a**, offsets the smaller amount of inductive stabilization. A subtle balance exists in each of the three anions and leads to the different geometries and the failure of linear free energy relationships.

The interaction between a charged site and a substituent directly bound to it depends to some degree on the particular system. First-row substituents ($N(CH_3)_2$, OCH_3, and F) do not affect the acidity of propene, but this observation cannot be generalized to every substrate; different compounds may display enhanced or even diminished acidities. Benzyl derivatives are analogous to the corresponding propenes,[40] but calculated deprotonation energies for substituted ethylenes and cyclopropanes are distinct, i.e. $F < OH < NH_2 < H$ (Table V).[41] The enhanced acidities can be accounted for simply by the electronegativity or field effect of the substituents. This contrasts with the propene data, and presumably is a result of the ions being localized and somewhat less flexible and having less repulsive electron–electron interactions. There is little experimental data, however, to compare the calculations to and consequently further discussion will be deferred until a later date.

Conclusions

Fragile anions which are weakly bound can be prepared at low temperatures under the unique conditions available in a flowing afterglow device. This makes it possible to study a series of 3-substituted propenes. The reactivity of the conjugate bases is generally in keeping with previous reports but occasionally leads to the formation of additional ions of interest, e.g. OHF^-. 3-Fluoropropene, 3-methoxypropene, and 3-(dimethylamino)propene have the same acidities, within experimental error, as the parent compound. Electron-withdrawing and π-donating substituents therefore do not destabilize an ion with respect to its basicity, but they do lead to a decrease in electron-binding energies. There is, however, an empirical correlation between acidity and electron affinity. Molecular orbital calculations reveal that the allylic anions (**4a**, **7a**, and **1a**) have different geometries as a result of a number of compensating factors. This explains why linear free energy relationships are not applicable in this case and suggests that different substrates may behave very differently. Ab initio computations support this latter notion and additional results will be reported in due course.

Acknowledgment. Support from the Minnesota Supercomputer Institute, University of Minnesota McKnight Land Grant Professorship program, National Science Foundation (CHE-8907198), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged.

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[39] Allyl anion (6-31+G* optimized structure) is planar and has a C–C bond distance of 1.388 Å and a C–C–C bond angle of 132.2°. Kroeker, R. L.; Bachrach, S. M.; Kass, S. R. *J. Org. Chem.* In press.

[40] Unpublished data, G. Dahlke and S. Kass.

[41] Previous ab initio calculations have been carried out. For example, see: (a) Tyrrell, J.; Kolb, V. M.; Meyers, C. Y. *J. Am. Chem. Soc.* **1979**, *101*, 3497. (b) Hopkinson, A. C.; McKinney, M. A.; Lien, M. H. *J. Comput. Chem.* **1983**, *4*, 513.

Carbene Thermochemistry from Collision-Induced Dissociation Threshold Energy Measurements. The Heats of Formation of $\tilde{X}^1A_1$ CF_2 and $\tilde{X}^1A_1$ CCl_2

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Abstract: The heats of formation of $\tilde{X}^1A_1$ CF_2 and $\tilde{X}^1A_1$ CCl_2 have been determined from measurements of the threshold energies for collision-induced halide ion dissociation from CF_3^- and CCl_3^- in a flowing afterglow–triple quadrupole apparatus. The derived values $\Delta H^\circ_{f,298}(CF_2, g) = -39.4 \pm 3.4$ kcal/mol and $\Delta H^\circ_{f,298}(CCl_2, g) = 52.1 \pm 3.4$ kcal/mol are significantly higher than the heats of formation recently obtained for these carbenes from proton affinity bracketing experiments by Lias, Karpas, and Liebman (*J. Am. Chem. Soc.* **1985**, *107*, 6089) but are in good agreement with measurements from other laboratories and with ab initio molecular orbital calculations. The gas-phase acidity (ΔH_{acid}) of $CHCl_3$ has also been determined from a proton-transfer bracketing procedure to be 357.6 ± 2.0 kcal/mol, from which $EA(CCl_3) = 2.25 \pm 0.10$ eV is obtained. The carbon–carbon bond energies in $CF_2{=}CF_2$ (79.1 ± 3.8 kcal/mol) and $Cl_2C{=}CCl_2$ (106.3 ± 4.9 kcal/mol) are derived from the present results and critically compared with the predicted values obtained from the proposed relationship between C=C bond strengths and carbene singlet–triplet energy gaps.

The modern era of carbene chemistry, according to Skell,[1] marks its beginnings with the pioneering kinetic studies by Hine and co-workers of CCl_2 intermediates in the alkaline hydrolysis of chloroform.[2] In the intervening 40 years since these seminal studies, interest in carbenes has grown across diverse chemical disciplines. The prodigious research activity devoted to carbenes is motivated not only by their practical utility in organic synthetic

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[1] Skell, P. S. *Tetrahedron* **1985**, *41*, 1427.

[2] Hine, J. *J. Am. Chem. Soc.* **1950**, *72*, 2438. Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964.

0002-7863/91/1513-5573$02.50/0 © 1991 American Chemical Society