with a variety of primary and secondary unsaturated alcohols (Table I). The results of reactions like eq 1 coupled with the observation that Wilkinson's catalyst could not be used in similar chemistry (vide infra) show that the use of a soluble oligomeric ligand is sufficient to kinetically isolate two mutually destructive species.

In a typical procedure, 3 mmol of unsaturated alcohol was dissolved in 10 mL of xylene along with a 4-fold excess of PVPCC and 0.03 mmol of the rhodium catalyst dispersed in polyethylene. This reaction mixture was heated to 100 °C for 18 h under hydrogen. A fairly rapid uptake of hydrogen was observed followed by a slower oxidation of the alcohol group. Alternatively, the oxidation was first accomplished at 70 °C for 15 h after which time heating to 100 °C dissolved the polyethylene and oligomerically ligated rhodium catalyst. In either case, the product ketone was separated from the spent oxidant and the Rh(I) catalyst by first cooling the reaction mixture to precipitate the Rh(I) catalyst and then filtering the resulting suspension. The mixture of rhodium catalyst and spent chromium oxidant was then extracted with hot toluene in a jacketed Soxhlet apparatus for 8 h under nitrogen and the toluene solution was cooled to recover the rhodium catalyst as a polyethylene dispersion. The rhodium catalyst could then be reused in a subsequent reaction.[10] In practice, the same sample of the rhodium catalyst was usable for up to three cycles at 100 °C. After about 40 h of exposure to PVPCC at 100 °C, the oligomeric Rh(I) catalyst was no longer active. At 70 °C the catalyst retained its activity. Decarbonylation of aldehydes was not a significant problem in the experiments in Table I. However, formation of a rhodium carbonyl by aldehyde decarbonylation is likely to eventually lead to catalyst deactivation in cases where aldehydes are produced. A control experiment (Table I) showed that ClRh(PPh₃)₃ could not be used in place of the oligomerically ligated rhodium catalyst in either of the procedures described above. Addition of Wilkinson's catalyst to a solution of an unsaturated alcohol followed by heating to effect oxidation of the alcohol led to no hydrogen uptake. After the alcohol oxidation was complete, analysis of the solution in this case showed triphenylphosphine oxide had formed. Thus, the insoluble oxidant oxidized both the Rh(I) and the triphenylphosphine ligand.

In summary, soluble, nonpolar alkene oligomers can be used to kinetically isolate one soluble species from a second insoluble species. The successful demonstration that a Rh(I) catalyst and its oxidation-sensitive phosphine ligands survive in the same reactor as a Cr(VI) oxidant suggests that such isolation procedures should be generally useful. In addition, by using oligomeric ligands prepared from ethylene oligomers, we can use entrapment in polyethylene to recover the catalyst at the end of a reaction cycle.

(10) Analysis by ICP of the solid residue from filtrates from hydrogenations using similar catalysts and 1-octene show that <0.1% of the charged rhodium catalyst was lost to solution during recovery of a poly(ethyldiphenylphosphine)-ligated rhodium catalyst by entrapment in a polyethylene precipitate.

On the Structure of the Allyl Anion

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This paper compares the geometry of the allyl anion deduced from photoelectron spectroscopic measurements[1] with structures calculated at reliable ab initio levels.[2-5] The serious discrepancies indicate that the experimental values are unlikely to be correct.

In a recent paper, Oakes and Ellison (OE) reported the photodetachment spectra of the allyl anion, $CH_2CHCH_2^-$, and of two deuterated species, $CH_2CDCH_2^-$ and $CD_2CDCD_2^-$.[1] The electron affinity of the parent ion (EA = 8.25 ± 0.5 kcal/mol) was lower than that of an earlier investigation (EA = 12.7 ± 1.2 kcal/mol)[6] but agreed (when combined with other known thermochemical values) with the proton affinity (PA = 391 ± 1) determined both by flowing afterglow methods[5] and by our earlier MP2/4-31+G//4-31+G calculations (see below).[2] However, analysis of the photoelectron spectra led OE to propose that the CCC angle in the allyl anion is 140 ± 4° and that the C–C bond lengths (r_0) are 1.505 Å for the parent anion and 1.555 and 1.612 Å for the deuterated species, respectively. All of these geometrical parameters appear to be much too large, as does the suggested substantial increase of 0.107 Å in the C–C bond lengths in going from $C_3H_5^-$ to $C_3D_5^-$. The Born–Oppenheimer potential energy surface is independent of isotopic substitution. While averages over the zero-point motions on this surface can vary, these differences generally are very small.[7]

Hückel theory makes a simple prediction.[8] Since the π HOMO of the allyl anion is nonbonding, the extent of occupation of this MO should not influence the C–C bond lengths significantly. The C–C bond orders in the allyl cation, the allyl radical, and the allyl anion are all 1.5, just as in benzene. To a first approximation, the C–C bond lengths in all four species should be very similar. This is exactly what has been indicated by earlier work[4,5] and is found by high-level calculations (summarized in Table I). We

(1) Oakes, J. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 7734–7741.

(2) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609–5612 and supplementary material. This was the first allyl anion calculation that employed full geometry optimization with an adequate (diffuse-function augmented) basis set. Also see: Schleyer, P. v. R.; Chandrasekhar, J.; Kos, A. J.; Clark, T.; Spitznagel, G. W. *J. Chem. Soc., Chem. Commun.* **1981**, *46*, 1693–1699.

(3) Full geometry optimizations without diffuse orbital-augmented basis sets: Boche, G.; Buckl, K.; Martens, D.; Schneider, D. R.; Wagner, H.-U. *Chem. Ber.* **1979**, *112*, 2961–2996. Cremoschi, P.; Morosi, G.; Simonetta, M. *J. Mol. Struct.* **1981**, *85*, 397–400. Pross, A.; DeFrees, D. J.; Levi, B. A.; Pollock, S. K.; Radom, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693–1699. Also see ref 5.

(4) Earlier, pioneering calculations on the allyl anion were not carried out with full geometry optimizations; e.g.: (a) Peyerimhoff, S. O.; Buenker, R. J. *J. Chem. Phys.* **1969**. (b) Boerth, D. W.; Streitwieser, A. *J. Am. Chem. Soc.* **1978**, *100*, 750. (c) For calculations on the methylallyl anion, radical, and cation, see: Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497–2501. (d) Also see: Elliott, R. J.; Richards, W. G. *J. Mol. Struct.* **1982**, *87*, 211–216 for MNDO geometries.

(5) McKay et al. (McKay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131–140) give $\Delta H_f{}^{\circ}{}_{298}$(allyl anion) = 29.0 ± 0.8 kcal/mol; the value OE deduced (29.5 ± 0.9 kcal/mol)[1] is in good agreement. From $\Delta H_f{}^{\circ}{}_{298}$(allyl radical) = 39.1 ± 1.5 kcal/mol recommended by McMillen et al. (McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532), EA_{298}(allyl) = 9.8 ± 2.4 kcal/mol.

(6) Zimmerman, D. H.; Brauman, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 3565–3568.

(7) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. L.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619–721.

(8) Heilbronner, E.; Bock, H. "Das HMO-Modell und seine Anwendung"; Verlag Chemie: Weinheim, 1968. Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemistry"; Wiley-Interscience: New York, 1961. For similar reasons, the CCC angle in the allyl cation is decreased over the values in the allyl radical or in propene (Table I).

Table I. Structural Details (r_e Values) of Allyl Species, C_{2v} Symmetry, and Comparison Molecules[a]

species	data source	C_1C_2	C_2H	C_1H_o	C_1H_i	$\angle CCC$	$\angle H_oC_1C_2$	$\angle H_iC_1C_2$
allyl cation	4-31G//4-31G[b]	1.371	1.070	1.073	1.074	119.4	121.4	121.9
	6-31G*//6-31G*[b]	1.373	1.073	1.076	1.076	118.1	121.5	121.6
allyl radical	MCHF/3-21G[c]	1.388	1.075	1.072	1.073	124.4	121.4	121.2
	UHF/4-31G//4-31G[b]	1.388	1.072	1.072	1.073	124.6	121.5	121.3
	UHF//6-31G*//6-31G*[d]	1.390	1.078	1.074	1.076	124.6	121.4	121.2
allyl anion	4-31G//4-31G[e]	1.380	1.090	1.078	1.075	133.0	121.2	122.1
	4-31+G//4-31+G[f]	1.387	1.085	1.076	1.077	131.6	121.1	121.8
	6-31+G*//6-31+G*[d][e]	1.388	1.087	1.078	1.080	132.2	120.8	121.9
benzene	3-21G//3-21G[b][g]	1.385	1.072			120.0	120.0	120.0
	6-31G//6-31G[h]	1.388	1.073			120.0	120.0	120.0
	6-31G*//6-31G*[g]	1.386	1.075			120.0	120.0	120.0
	exptl[i]	1.396	1.085			120.0	120.0	120.0
propene	4-31G//4-31G[b][j]	1.318	1.076	1.072	1.074	123.3	121.9	121.9
	6-31G*//6-31G*[b][j]	1.318	1.079	1.077	1.076	125.3	121.8	121.7
	exptl[j][k]	1.336	1.090	1.081	1.091	124.3	121.5	120.5

[a] Angles in degrees, distances in angstroms. The hydrogens at C_1 are designated H_o ("out", syn to $H(C_2)$) and H_i ("in", anti to $H(C_2)$). The standard Pople basis set designations are employed; geometries were fully optimized at these levels. The largest basis sets (6-31G* or 6-31+G*), in general, are expected to give the most accurate results.[13] [b] "The Carnegie-Mellon Quantum Chemistry Archive", 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie-Mellon University: Pittsburgh, PA, 1983. [c] Reference 10. [d] Present work. [e] Reference 3. [f] Reference 2. [g] Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500–7505. [h] Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289–298. This paper gives references to earlier theoretical studies. [i] Tomagawa, K.; Ijimura, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243. Nearly identical values are reported by: Cabona, A.; Bachand, J.; Giguere, J. *Can. J. Phys.* **1974**, *52*, 1949 ($r_0 = 1.396$, 1.083 Å). Oldani, M. Bauder, A. *Chem. Phys. Lett.* **1984**, *108*, 7 ($r = 1.395$, 1.082 Å). In the earlier references cited in these papers. [j] Other values at 4-31G, 6-31G*, and exptl, respectively: C_2C_3, 1.500, 1.503, 1.501; av C_3H's, 1.084, 1.086, 1.094; HC_2C_1, 119.2, 119.1, 116.7; H (ecl)C_3C_2, 111.4, 111.5, 111.2. [k] Reference 7.

conclude that the C–C bond length in the allyl anion is unlikely to differ by more than 0.02 Å from the best calculated value, r_e = 1.388 Å (6-31+G*//6-31+G*). In contrast, the range of distances deduced experimentally, 1.505–1.612 Å, suggests an essentially single bond between carbon atoms. This is difficult to rationalize on any theoretical basis.

However, the degree of π-orbital occupancy influences the geometry in another way. Early calculations on the allyl anion, although carried out with only partial geometry optimization, revealed a significant widening of the CCC angle.[4] This can reasonably be attributed to 1,3-repulsion between the out-of-phase p orbitals in the allyl anion HOMO.[8] The implications of such angle widening for the interpretation of NMR spectra of organometallic allyl derivatives has been discussed in detail in recent publications.[9] On the basis of their analysis, Oakes and Ellison concluded that the bond angle change between the allyl anion and the allyl radical is 16 ± 4°.[1] On the basis of 124° bond angle of the allyl radical calculated by Takeda and Dupuis,[10] a value of 140 ± 4° for <CCC in $C_3H_5^-$ was proposed. OE noted that some of the earlier calculations on the allyl anion gave a smaller value, about 133°,[4] but reiterated the opinion "that accurate calculations on weakly bound negative ions are quite difficult".

We demonstrated in 1981 that calculations on negatively charged species are not difficult at all, provided diffuse functions are included in the basis set.[2] It has been known for some time[2,11] that the outer electrons in isolated anions are not strongly bound, so that basis sets that describe neutral and positively charged species adequately are not appropriate for their negatively charged counterparts. Our relatively simple 4-31+G[2] and 3-21+G[11] basis sets give quite good results with anions and have now come into general use. Specifically, the MP2/4-31+G//4-31+G proton affinity of the allyl anion, 391 kcal/mol (after correction by 8 kcal/mol for the zero point energy differences),[2] is in perfect agreement with experiment. Earlier calculations on anions, which did not include diffuse functions on the basis set, gave unsatisfactory energetic results.[3-5]

The optimized 4-31+G geometry of the allyl anion indicated a CCC bond angle of 131.6°, i.e., only widened by 8° from the allyl radical value (Table I). This is only half the widening

deduced by OE. To corroborate this result, we have now optimized the allyl anion geometry at the 6-31+G* basis set level.[12] This split-valence basis set augmented by diffuse and d-type polarization functions on all carbon atoms gives <CCC = 132.2° and r_e = 1.388 Å (Table I). On the basis of extensive comparisons of calculated (6-31G* basis set) with reliable (microwave) experimental geometries of neutral species (cf. the data for C_6H_6 and C_3H_6 indicated in Table I), errors in bond lengths on the order of 0.02 Å and in bond angles of ±2° are to be expected.[13] These errors tend to be even less for hydrocarbons and are not likely to be greater for the allyl anion.[14]

The experimental determination of the structure of multiatomic charged species is an exciting and difficult challenge for spectroscopists.[15] Nevertheless, it is much easier at present to calculate such species theoretically at whatever level of sophistication the available programs and computer time permit. Since the accuracy of such calculations on larger systems is often considerably greater than that currently achievable experimentally, advantage should be taken of computational methods to assist experimental studies and to test conclusions.

Note Added in Proof. Prof. Ellison has now conceded (private communication) that only the deviation of the allyl anion CCC angle from the allyl radical value can be deduced directly from their data. However, this deviation is twice as large as that calculated here.

(9) Clark, T.; Rhode, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344. Decher, G.; Boche, G. *J. Oganomet. Chem.* **1983**, *259*, 31.

(10) Takeda, T.; Dupuis, T. *J. Am. Chem. Soc.* **1983**, *105*, 1713–1716.

(11) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301.

(12) The GAUSSIAN82 Program, with the standard basis sets, was employed: Binkley, J. S.; Frisch, M.; Raghavachari, K.; De Frees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A., Release A, VAX Version, Carnegie-Mellon University.

(13) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. "Ab Initio Molecular Orbital Theory"; Wiley-Interscience: New York, 1985. Further increases in accuracy are achieved at electron correlated levels.

(14) At 6-31+G*, the electron affiity of the allyl radical is calculated to be 6.00 kcal/mol larger than that of methyl by the following equations: C_3H_5 (−116.472 59 au) + CH_3^- (−39.504 15) → $C_3H_5^-$ (−116.425 20) + CH_3 (−39.561 10). Combined with the experimental EA(CH_3) = 1.8 ± 0.7 eV (Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556–2558), this gives EA(C_3H_5) = 7.8 ± 0.7 eV in agreement with the experimental value, 8.35 ± 0.5 eV, determined in ref 1.

(15) Miller, T. A.; Bondybey, V. E., Eds. "Molecular Ions: Spectroscopy, Structure, and Chemistry"; North Holland Publishing Co., Amsterdam, 1983.