these bases leads to an increase in bond distances. Bond angles increase in going from the anion to the neutral base and to the protonated base.

Registry No. NH_4^+, 14798-03-9; OH^-, 14280-30-9; H_3O^+, 13968-08-6; H_2F^+, 12206-67-6; PH_2^-, 13937-34-3; PH_4^+, 16749-13-6; HS^-, 15035-72-0; H_3S^+, 18155-21-0; H_2Cl^+, 36658-55-6; CN^-, 57-12-5; $HCNH^+$, 21107-92-6.

Theoretical Predictions of Activation Energies for 1,2-Hydrogen Shifts in Singlet Carbenes[†]

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Activation energies for 1,2-hydrogen shifts of substituted methylcarbenes are predicted using MP4/6-311G** energies calculated on MP2/6-31G* optimized geometries. An excellent linear free energy correlation is observed between predicted activation energies and the σ_R° values of the α-substituents. Activation barriers for the 1,2-hydrogen shift of methylcarbene, methylchlorocarbene, cis- and trans-methylhydroxycarbene, cis- and trans-methylmethoxycarbene, trans-methylvinylcarbene, and allylcarbene are predicted and compared with experimental values, when available.

Introduction

Recent studies of intramolecular 1,2-hydrogen shifts,[1] and the determination of activation parameters for additions and cyclo-additions of substituted alkylcarbenes,[2] prompt us to report our theoretical investigations of such processes. Substituents directly attached to the carbene carbon have large effects on activation energies for 1,2-hydrogen migrations to this center,[1,2] and substitution of the migration origin may also have an effect on reactivity.[3] For simple systems, activation barriers are predicted to range from zero to substantially positive values depending upon the level of theory and substituents involved.[4] We have studied a number of systems and have found a linear free energy correlation between activation energy and σ_R° values for α-substituents.

Background

The isomerizations of simple alkylcarbenes are so rapid that intermolecular interception with unsaturated species has not yet been achieved. The rearrangement of vinylidene to acetylene was studied theoretically most recently by both Pople[5] and Schaefer.[6] The predicted barrier is much too large at the Hartree–Fock level but becomes 0.9 kcal/mol when calculated with large basis sets, inclusion of electron correlation, and zero point energy corrections. No direct evidence is available for the existence of vinylidene, but Lineberger's group reported vibrational structure in the photoelectron spectrum of vinylidene anion and suggested that there is a significant barrier to the formation of acetylene.[7] Trapping with 2-butene provides evidence that dimethylvinylidene exists.[8]

The existence of singlet methylcarbene is uncertain.[9] Various theoretical treatments of the rearrangement of methylcarbene to ethylene are summarized in Table I. The MP4SDQ/6-31G** level of theory is generally accepted as leading to good agreement with studies using coupled cluster theory with double substitutions (CCD) with similar basis sets.[10] The MP4 level of theory predicts a 2.6 kcal/mol barrier. Corrections to the MP4SDQ/6-31G** energy with triple substitutions in the fourth-order Møller–Plesset perturbation treatment (Δ_1) and the expansion from a double to triple-split-valence s,p-basis set (Δ_2) placed the singlet ground state of methylcarbene 1.1 kcal/mol above the 1,2-shift transition state.[5]

TABLE I: Calculated Activation Barriers for the 1,2-Hydrogen Shift in Methylcarbene (Absolute Energies of the Carbene in hartrees and Activation Energy and Zero Point Energy Correction in kcal/mol)

level of theory	ref	$H_3C\ddot{C}$	ΔE^*
MINDO/2	a		0.0
MINDO/3	b		0.7
MNDO	b		21.9
AM1	c	0.13970	14.9
ab initio double ζ	d		20.9
double ζ	e		27.0
RHF/3-21G	c	−77.48509	20.8
RHF/4-31G	f	−77.80416	19.9
RHF/6-31G* = HF	c	−77.92237	13.4
RHF/6-31G* ZPE	c	33.7	−0.9
MP2/6-31G* = MP	c	−78.16206	1.8
MP3/6-31G*//MP	c	−78.18898	4.0
MP4/6-31G*//MP	c	−78.20105	3.2
MP2/6-311G**//MP	c	−78.25318	0.1
MP3/6-311G**//MP	c	−78.28456	2.4
MP4SDQ/6-31G**//HF	a	−78.21961	2.6
MP4SDQ/6-31G**//HF + Δ_1 + Δ_2[g]	a		−1.1
MP4/6-311G**//MP	c	−78.29783	1.5
MP4/6-311G**//MP + ZPE	c		0.6

[a] Reference 5c. [b] Reference 18b. [c] This work. [d] Reference 18d. [e] Reference 18c. [f] Reference 4d. [g] Δ_1 = E(MP4SDTQ/6-31G*) − E(MP4SDQ/6-31G*) and Δ_2 = E(MP2/6-311G**) − E(MP2/6-31G**).

Thus, the activation energy is essentially zero for the reaction. Only recently, the barrier for the 1,2-hydrogen shift in a di-

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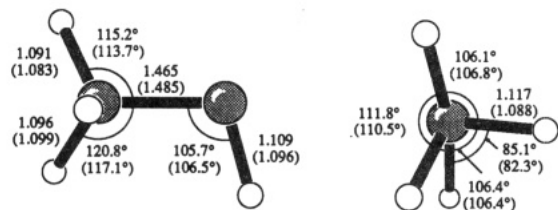
Figure 1. Two views of the MP2/6-31G* structure of methylcarbene. RHF/6-31G* values are in parentheses.

Figure 2. Three views of the MP2/6-31G* transition structure for the 1,2-hydrogen shift of methylcarbene to ethylene. RHF/6-31G* values are in parentheses.

Figure 3. Two views of the MP2/6-31G* structure of methylchlorocarbene.

alkylcarbene has been estimated as 1.1 ± 1 kcal/mol.[1f] This was accomplished by examining the products from the thermolysis of 4-diazirinopentanoic acid.

Substituents have a dramatic influence on reactivity. Moss et al. have shown an enhancement of stability and supression of reactivity for halogen-substituted carbenes.[11] Liu and co-workers have reported the absolute rate constants and activation barriers for the 1,2-hydrogen migration in both benzylbromocarbene (E_a = 4.7 ± 2 kcal/mol)[1g,h] and benzylchlorocarbene (E_a = 6.4 ± 2 kcal/mol[1h] and 4.83 ± 0.24[1d,j]). The rate constants[1b] and activation energies[1e] for the 1,2-hydrogen shifts in various alkylhalocarbenes have also been reported. The activation barriers of methyl-chlorocarbene, ethylchlorocarbene, and isopropylchlorocarbene are reported from time-resolved photoacoustic calorimetry as 4.9 ± 0.5, <2.4, and <2.4 kcal/mol, respectively.[1e]

Activation parameters have recently been computed with the MNDO and MINDO/3 methods.[1b] The computed activation barriers for methylchlorocarbene and benzylchlorocarbene were overestimated by MNDO (30.3 and 26.1 kcal/mol), whereas MINDO/3 yields more reasonable activation energies of 9.4 and 4.3 kcal/mol.

Theoretical Methods

All calculations were carried out with GAUSSIAN 86.[12,13] Op-

TABLE II: Calculated Activation Barriers for the 1,2-Hydrogen Shift in Methylchlorocarbene

level of theory	$H_3C\ddot{C}Cl$	ΔE^*
AM1	0.093 10	24.6
MNDO[a]		30.3
MINDO/3[a]		9.4
RHF/3-21G	−534.222 58	28.4
RHF/6-31G*	−536.847 44	23.3
RHF/6-31G* ZPE	29.6	−1.9
MP2/6-31G* = MP	−537.233 58	13.6
MP3/6-31G*//MP	−537.265 02	16.0
MP4/6-31G*//MP	−537.284 37	15.8
MP2/6-311G**//MP	−537.386 24	11.0
MP3/6-311G**//MP	−537.420 49	13.6
MP4/6-311G**//MP	−537.442 45	13.4
MP4/6-311G**//MP + ZPE		11.5

[a] Reference 1b.

timized geometries were determined using RHF theory with the 3-21G or 6-31G* basis sets[14,15] and also with the MP2/6-31G* level of theory. Single point energy calculations employed fourth-order Møller–Plesset perturbation theory[16] including triple substitution using the 6-31G* and 6-311G** basis sets[17] and are designated MP4 in the tables rather than the traditional MP4SDTQ. Møller–Plesset calculations include the full core.

Results and Discussion

The stationary point geometries of the methylcarbene rearrangement were located at the MP2/6-31G* level. The energies

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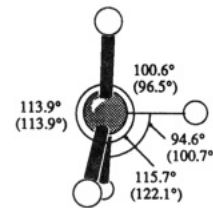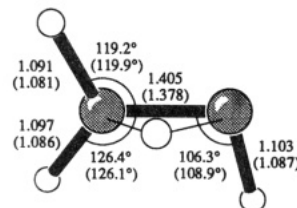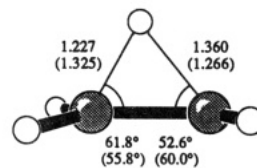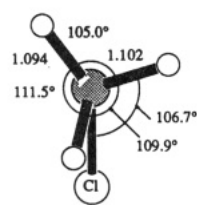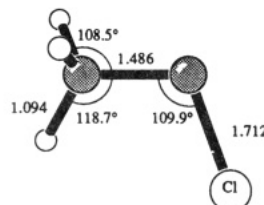
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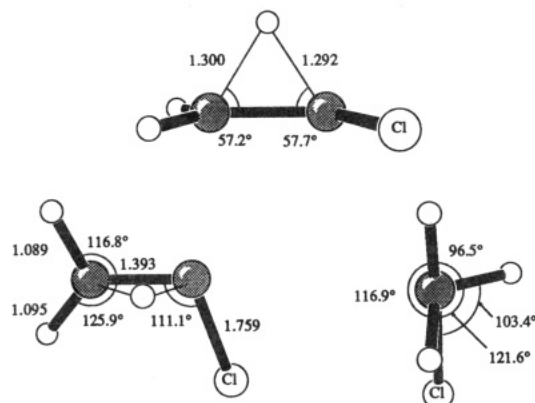
Figure 4. Three views of the MP2/6-31G* transition structure for the 1,2-hydrogen shift of methylchlorocarbene to chloroethylene.

were computed with a triple-split-valence basis, and the correlation energy was computed at the MP4 level including triple substitution. These data are presented in Table I, along with earlier results. The MP2/6-31G* and MP4/6-311G** energies are accidentally very similar. The MP2 value overestimates the MP4 activation energy by only 0.3 kcal/mol. Subsequent calculations where the larger MP4 calculations are not possible are corrected by this amount (cf. methylmethoxycarbene and methylvinylcarbene). The MP2/6-31G* activation barrier for the methylcarbene rearrangement is 0.9 kcal/mol, with zero point corrections. Our final estimation using the 6-311G** basis, full-MP4 treatment, and zero point energy corrections predicts an activation energy of 0.6 kcal/mol.

The MP2/6-31G* and RHF/6-31G* geometries of the ground and transition structures of methylcarbene are shown in Figures 1 and 2. Both RHF structures are consistent with the geometries in earlier studies.[18] The ground-state species has similar RHF and MP2 geometries. The only significant difference is in the computed angle between the hydrogen best aligned for migration and the carbene carbon. The MP2 value is 93°, 8° smaller than predicted for RHF. Pronounced differences are observed for the transition structure of the rearrangement. The MP2 structure reflects an earlier transition state, as shown by the two carbon-hydrogen distances involved with the migrating center. The migration origin and terminus distances are 1.227 and 1.360 Å for MP2, with RHF yielding distances of 1.325 and 1.266 Å, respectively. It is this ratio, or position of the transition state along the potential surface, which presents the difference between our current work and that of Krishnan et al. in predicting the activation energy of the methylcarbene rearrangement. The MP2 geometry is intutively satisfying, since an early transition state is predicted for an exothermic reaction requiring relatively small activation energy by the Hammond postulate.[19]

Methylchlorocarbene was treated at the same levels as methylcarbene (Table II). The final estimate of the activation energy for the 1,2-hydrogen shift in methylchlorocarbene is 11.5 kcal/mol. LaVilla et al. have recently published an experimental activation energy for the 1,2-hydrogen shift in methylchlorocarbene.[1e] Our estimate for this process is quite sizable (11.5 kcal/mol) as compared to 4.9 kcal/mol from time-resolved photoacoustic calorimetry.

The MP2/6-31G* geometries of the ground and transition structures of methylchlorocarbene are shown in Figures 3 and 4. The ground-state conformation differs from that of methylcarbene. This is illustrated by comparing the dihedral angle defined by the carbene substituent, carbene center, sp^3 carbon, and the hydrogen

TABLE III: Calculated Activation Barriers for the 1,2-Hydrogen Shift in *trans*-Methylhydroxycarbene[a]

level of theory	*trans*-H$_3$CC̈OH	$\Delta E^{\ast}$
AM1	0.002 83	34.7
RHF/3-21G	−151.979 58	43.9
RHF/6-31G*	−152.832 91	38.7
RHF/6-31G* ZPE	39.8	−2.5
MP2/6-31G* = MP	−153.262 42	27.8
MP2/6-311G**//MP	−153.411 02	25.2
MP3/6-311G**//MP	−153.434 68	27.5
MP4/6-311G**//MP	−153.461 56	27.0
MP4/6-311G**//MP + ZPE		24.5

[a] Both the ground and transition states are in the trans conformation.

TABLE IV: Calculated Activation Barriers for the 1,2-Hydrogen Shift in *cis*-Methylhydroxycarbene[a]

level of theory	*cis*-H$_3$CC̈OH	$\Delta E^{\ast}$
AM1	−0.001 80	37.0
RHF/3-21G	−151.971 84	44.1
RHF/6-31G*	−152.825 52	39.2
RHF/6-31G* ZPE	39.4	−2.4
MP2/6-31G* = MP	−153.256 62	28.0
MP2/6-311G**//MP	−153.404 35	25.3
MP3/6-311G**//MP	−153.428 03	27.9
MP4/6-311G**//MP	−153.455 23	27.3
MP4/6-311G**/MP + ZPE		24.9

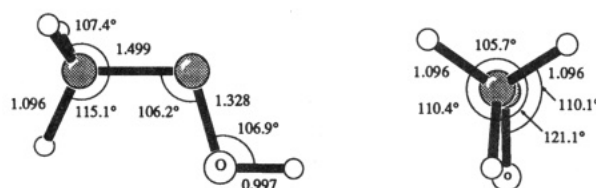[a] Both the ground and transition states are in the cis conformation.

Figure 5. Two views of the MP2/6-31G* structure of methylhydroxycarbene.
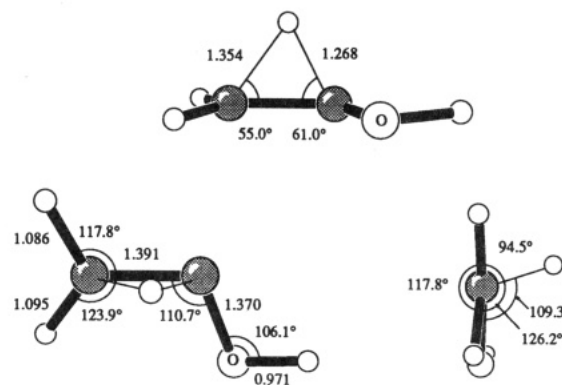

Figure 6. Three views of the MP2/6-31G* transition structure for the 1,2-hydrogen shift of methylhydroxycarbene to vinyl alcohol.

best located for the 1,2 migration. For methylcarbene, the dihedral angle is 85.1° (Figure 1), while for methylchlorocarbene it is 106.7°, as shown in Figure 3. The transition structure, Figure 4, is further along the reaction coordinate than methylcarbene, consistent with the lower exothermicity of the reaction. The migration origin and terminus distances are 1.300 and 1.292 Å, which differ substantially from the values for the methylcarbene transition structure.

Another system of interest, methylhydroxycarbene, has been investigated by other workers.[20] Both *cis*- and *trans*-methylhydroxycarbene were studied at the same levels of theory as others in the study (Tables III and IV). The trans conformer is the lower energy species for both the ground and transition states. At the

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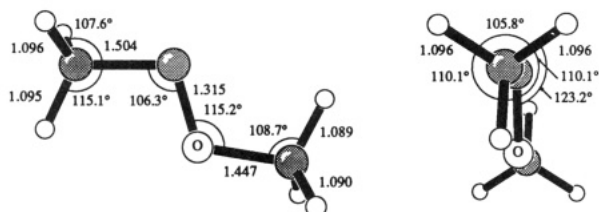(20) Yadav, J. S.; Goddard, J. D. *J. Chem. Phys.* **1986**, *85*, 3975.

Figure 7. Two views of the MP2/6-31G* structure of methylmethoxycarbene.
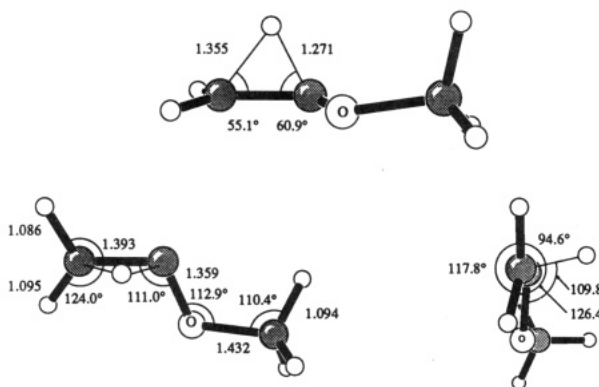

Figure 8. Three views of the MP2/6-31G* transition structure for the 1,2-hydrogen shift of methylmethoxycarbene to methyl vinyl ether.

TABLE V: Calculated Activation Barriers for the 1,2-Hydrogen Shift in *trans*-Methylmethoxycarbene[a]

level of theory	*trans*-H$_3$CCOMe	$\Delta E^{\ddagger}$
AM1	0.012 95	32.9
RHF/3-21G	−190.792 56	45.1
RHF/6-31G*	−191.860 19	39.6
RHF/6-31G* ZPE	59.3	−2.3
MP2/6-31G*	−192.423 92	29.5
MP2/6-31G* + ZPE		27.2
MP2/6-31G* + ZPE + MP4 correction[b]		26.9

[a] Both the ground and transition states are in the trans conformation. [b] Corrected for the energy difference between the computed MP4/6-311G** and MP2/6-31G* values of the methylcarbene rearrangement to ethylene.

TABLE VI: Calculated Activation Barriers for the 1,2-Hydrogen Shift in *cis*-Methylmethoxycarbene[a]

level of theory	*cis*-H$_3$CCOMe	$\Delta E^{\ddagger}$
AM1	0.006 66	36.8
RHF/3-21G	−190.780 37	42.2
RHF/6-31G*	−191.845 23	36.5
RHF/6-31G* ZPE	59.2	−2.2
MP2/6-31G*	−192.410 43	25.6
MP2/6-31G* + ZPE		23.4
MP2/6-31G* + ZPE + MP4 correction[b]		23.1

[a] Both the ground and transition states are in the cis conformation. [b] Corrected for the energy difference between the computed MP4/6-311G** and MP2/6-31G* values of the methylcarbene rearrangement to ethylene.

TABLE VII: Calculated Activation Barriers for the 1,2-Hydrogen Shift in *trans*-Methylvinylcarbene[a]

level of theory	H$_3$CCCH=CH$_2$	$\Delta E^{\ddagger}$
AM1	0.145 86	17.4
RHF/3-21G	−153.958 05	28.5
RHF/6-31G*	−154.823 92	22.4
RHF/6-31G* ZPE	58.6	−1.9
MP2/6-31G*	−155.326 11	10.6
MP2/6-31G* + ZPE		8.7
MP2/6-31G* + ZPE + MP4 correction[b]		8.4

[a] Both the ground and transition states are in the trans conformation. [b] Corrected for the energy difference between the computed MP4/6-311G** and MP2/6-31G* values of the methylcarbene rearrangements to ethylene.

TABLE VIII: Calculated Activation Barriers for the 1,2-Hydrogen Shift in Allylmethylene

level of theory	HCCH$_2$CH=CH$_2$	$\Delta E^{\ddagger}$
AM1	0.169 21	12.5
RHF/3-21G	−153.935 86	15.3
RHF/6-31G*	−154.801 33	8.0
RHF/6-31G* ZPE	57.6	−1.0
RHF/6-31G* + ZPE		7.0
RHF/6-31G* + ZPE + estimation[a]		0.0

[a] The estimation is derived from the difference in activation energy for the methylcarbene rearrangement computed at the RHF/6-31G* and MP4/6-311G** levels of theory (11.9 kcal/mol).
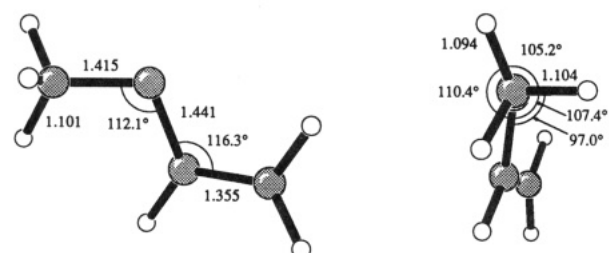

Figure 9. Two views of the MP2/6-31G* structure of methylvinylcarbene.

highest level of theory the trans transition state is predicted to be 0.4 kcal/mol lower than the corresponding cis transition structure. The activation energy for rearrangement of the trans conformer is 24.5 kcal/mol, consistent with experimental suppression of the 1,2-hydrogen shift that has been observed.[21]

The ground and transition structures of *trans*-methylhydroxycarbene are shown in Figures 5 and 6. A nonmigrating CH bond is eclipsed with the CO bond. The transition structure also gives the most unequal migrating hydrogen distances so far examined. The migration origin and terminus distances are 1.354 and 1.268 Å.

Comparison of the MP2/6-31G* activation energies with the MP4/6-31G** single points with methylcarbene, methylchlorocarbene, and methylhydroxycarbene show quite satisfactory agreement between the two. The MP2/6-31G* energies are found to be 0.3, 0.2, and 0.8 kcal/mol higher than those predicted by MP4. Therefore, only MP2/6-31G* optimizations, with no higher level single point energy calculations, were carried out on the larger *cis*- and *trans*-methylmethoxycarbene and *trans*-methylvinylcarbene.

The ground and transition structures are presented in Figures 7 and 8 for methylmethoxycarbene. The trans ground-state species is a C_s symmetric minimum. The transition state is similar to that of methylhydroxycarbene, in that the ratio of distances for the migrating center indicate a late transition state. For me-

thylmethoxycarbene the trans conformer is predicted to be the more stable transition structure. The activation energy, including zero point corrections, is found to be 27.2 kcal/mol (Tables V and VI). The corresponding cis migration activation energy is 23.4 kcal/mol with respect to the cis ground state. The MP2 to MP4 correction lowers these to 26.9 and 23.1 kcal/mol, respectively.

Finally, to investigate the effect of π-conjugation upon the 1,2 shift, stationary points for *trans*-methylvinylcarbene were also located, as shown in Table VII. The π-system provides stabilization of the carbene, yielding a 8.7 kcal/mol barrier, which is 6.9 kcal/mol above that of methylcarbene (MP2/6-31G*). The corrected activation barrier is 8.4 kcal/mol. The ground and transition structures are shown in Figures 9 and 10. An interesting
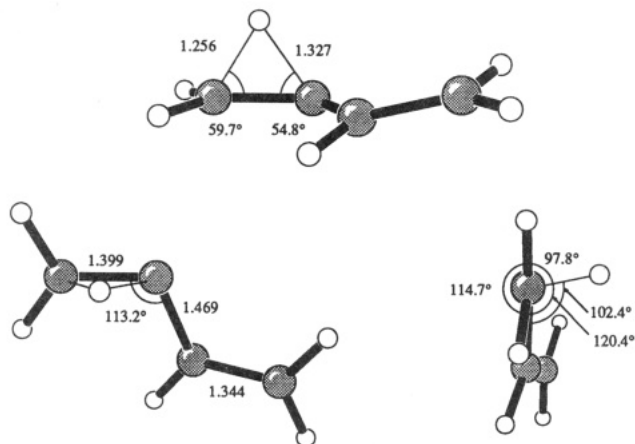
(21) Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1965**, 1700.

Figure 10. Three views of the MP2/6-31G* transition structure for the 1,2-hydrogen shift of methylvinylcarbene to 1,3-butadiene.

TABLE IX: Comparison of Computed and Experimental Activation Energies for Substituted Alkylcarbenes

system	$\Delta E^{\ddagger}$ + ZPE theory[a]	$\Delta E^{\ddagger}$ experimental
CH$_2$Ç	0.9[b]	
CH$_3$ÇH	0.6	
CH$_3$ÇCl	11.5	4.9 ± 0.5[h]
CH$_3$CH$_2$ÇCl		<2.4[h]
(CH$_3$)$_2$CHÇCl		<2.4[h]
CH$_3$ÇOH(*trans*)	24.5	
CH$_3$ÇOH(*cis*)	24.9	
CH$_3$ÇOMe(*trans*)	27.2	
CH$_3$ÇOMe(*cis*)	23.4	
CH$_3$ÇCHCH$_2$	8.7	
HÇCH$_2$CHCH$_2$	0.0[i]	
CH$_3$ÇF	19[c]	
Ph-CH$_2$ÇBr		4.7 ± 2[d]
Ph-CH$_2$ÇCl	6.0[i]	6.4 ± 2;[e] 4.83 ± 0.24[j]
CH$_3$ÇCH$_2$CO$_2$H		1.1 ± 1[f,g]

[a] This work, unless specified otherwise. [b] Reference 5a. [c] Reference 23 and a 0.9 kcal/mol correction for basis set correction and 0.9 kcal/mol for ZPE (see text). [d] Reference 1g. [e] Reference 1h. [f] Reference 1f. [g] Estimation of probable value. [h] Reference 1e. [i] Corrected theoretical estimate from this work, see text. [j] Reference 1d and 1g.

feature that holds for both the ground and transition structures of methylvinylcarbene is that the carbon framework is perturbed out of plane by a 16° rotation about the central CC bond (Figure 10). The migrating origin and terminus distances are 1.256 and 1.327 Å in the transition structure, which are very close to the values in methylcarbene.

We have tabulated (Table IX) the available experimental activation energies from the literature, along with those obtained from our theoretical work. There is an obvious relationship between the activation energy for migration and the stabilization of the carbene by electron donation from substituents attached to the carbene carbon. This relationship is shown more clearly by a plot of the activation energies of the substituted methylcarbenes versus the electron-donating abilities of the substituents, measured by Hammett–Taft substituent constants σ_R°. These constants are a classical measure of electron release.[22] This relationship is illustrated in Figure 11, and the σ_R° parameters are given in Table X.

Most experimental activation parameters are reported for benzylhalocarbenes. We have chosen allylcarbene to elucidate the effect of a β-vinyl group on carbene reactivity. The vinyl group serves as a simple model for the phenyl group. The optimization was carried out at the RHF/6-31G* level of theory. The MP2/6-31G* transition structure could not be located easily, so
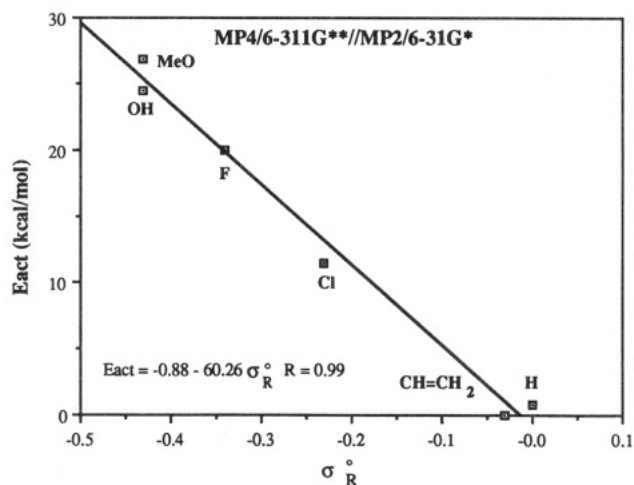
(22) Hansch, C.; Leo, A. J. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.

Figure 11. Correlation between computed activation barriers and the Hammett–Taft substituent constants, σ_R°, for α-substituents.

TABLE X: Substituent Parameters

substituent	σ_R°	substituent	σ_R°
OMe	−0.43[a]	Cl	−0.23[b]
OH	−0.43[a]	CH$_3$	−0.13[a]
F	−0.34[b]	C$_2$H$_3$	−0.03[a]

[a] Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Andersen, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 3146. [b] Brownlee, R. T. C.; Hutchinson, R. E. J.; Katritzky, A. R.; Tidwell, T. T.; Topsom, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 1757.

that the effect is rationalized on the basis of RHF/6-31G* results. The activation barrier for the 1,2 shift is 7.0 kcal/mol at the RHF/6-31G* + ZPE level. This is 5.5 kcal/mol less than the methylcarbene activation energy of 12.5 kcal/mol at the same level of theory. From this it may be reasonable to assume that the effect of the β-phenyl group will be to lower the barriers of 1,2 shifts on the order of 5.5 kcal/mol. This leads to a prediction of an activation energy of 6.0 kcal/mol for benzylchlorocarbene, in excellent accord with the experimentally determined values of 6.4 ± 2[1h] and 4.83 ± 0.24[1d,j] kcal/mol. It also suggests that the barrier to hydrogen shift in allylmethylene will be nonexistent.

The 1,2-hydrogen shift of methylfluorocarbene is reported by Dailey to have an activation energy of 21 kcal/mol.[23] The activation energy was determined with the MP4/6-31G** basis set on MP2/6-31G* optimized geometries. To compare with our MP4/6-311G** results, we subtract the 0.9 kcal/mol difference between the MP2/6-311G** and MP2/6-31G** activation energies for the methylcarbene rearrangement.[5c] When also corrected by the zero point energy (0.9 kcal/mol), a predicted activation energy of 19 kcal/mol is obtained.

As shown in Figure 11, the corrected energy of activation correlates with σ_R° parameters. These parameters are an empirically derived measure of the electron-donor ability of substituents. Electron donors stabilize the carbenes more than they stabilize the transition states.

Conclusion

The 1,2-hydrogen shift is predicted to have an activation barrier of 0.6 kcal/mol for singlet methylcarbene. A linear correlation between activation energy and the σ_R° substituent constants has been found. Substitution at either the α- or β-positions influences carbene reactivity. The predicted activation energies for methylchlorocarbene, *cis*- and *trans*-methylhydroxycarbene, *cis*- and *trans*-methylmethoxycarbene, *trans*-methylvinylcarbene, and allylmethylene are 11.5, 24.9, 24.5, 23.1, 26.9, 8.4, and 0.0 kcal/mol.

(23) Personal communication with Professor William Dailey of the University of Pennsylvania.

Reaction Path Following in Mass-Weighted Internal Coordinates

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Our previous algorithm for following reaction paths downhill (*J. Chem. Phys.* **1989,** *90,* 2154), has been extended to use mass-weighted internal coordinates. Points on the reaction path are found by constrained optimizations involving the internal degrees of freedom of the molecule. The points are optimized so that the segment of the reaction path between any two adjacent points is described by an arc of a circle in mass-weighted internal coordinates, and so that the gradients (in mass-weighted internals) at the end points of the arc are tangent to the path. The algorithm has the correct tangent vector and curvature vectors in the limit of small step size but requires only the transition vector and the energy gradients; the resulting path is continuous, differentiable, and piecewise quadratic. Reactions paths for $CH_4 + H \rightarrow CH_3 + H_2$, $HCN \rightarrow CNH$, $F^- + CH_3F \rightarrow FCH_3 + F^-$, and $C_2H_5F \rightarrow C_2H_4 + HF$ are calculated and the results are compared to the paths obtained with mass-weighted Cartesians and with internal coordinates without mass-weighting.

1. Introduction

The concept of the reaction pathway has become important in the study of potential energy surfaces for chemical reactions. In general, the reaction path can be defined as the curve on the potential energy surface connecting the reactants and products through the transition state. This curve can be found by following the steepest descent path or minimum energy path (MEP) from the transition state toward reactants and products. When mass-weighted Cartesian coordinates are used, the path becomes the intrinsic reaction coordinate (IRC) discussed by Fukui.[1]

In a previous paper, a new reaction path algorithm was presented that is capable of following curved reaction paths with reasonable large step sizes.[2] The efficiency and stability of the method was demonstrated on a model surface and various simple reactions by using internal coordinates without mass-weighting. To study reaction dynamics, it is desirable to include mass-weighting in the determination of the reaction path.

In the present work, our previous algorithm[2] is modified to include the effects of the atomic masses. The new algorithm for following the intrinsic reaction coordinate in mass-weighted internal coordinates is tested on the following reactions: $CH_4 + H \rightarrow CH_3 + H_2$, $HCN \rightarrow HNC$, $F^- + CH_3F \rightarrow FCH_3 + F^-$, and $C_2H_5F \rightarrow C_2H_4 + HF$. The resulting reaction paths are compared with the paths obtained with the non-mass-weighted algorithm.

2. Theory

The steepest descent path in mass-weighted Cartesian coordinates (IRC) corresponds to the path obtained by stepping in the direction of the instantaneous acceleration. For other coordinate systems, the IRC can be obtained by transforming the steepest descent path in mass-weighted Cartesian coordinates. Entirely equivalently, the IRC can be constructed by following the instantaneous acceleration vector given by the equations of motion in that coordinate system.

The potential energy surface near the reaction path can be expanded as a Taylor series in internal coordinates

$$E(\mathbf{q}) = E'(\mathbf{q}') + \mathbf{g}^t \Delta \mathbf{q} + \frac{1}{2} \Delta \mathbf{q}^t \mathbf{H}_q \Delta \mathbf{q} + \dots \qquad (1)$$

where $\Delta \mathbf{q} = \mathbf{q} - \mathbf{q}'$, $\mathbf{H}_q$ is the Hessian matrix in internal coordinates and $\mathbf{g}$ is the gradient vector.

The classical kinetic energy in internal coordinates can be written as

$$2T = \Delta \dot{\mathbf{q}}^t \mathbf{G}^{-1} \Delta \dot{\mathbf{q}} \qquad (2)$$

where T is the kinetic energy, $\mathbf{G}^{-1}$ is the inverse of the Wilson G matrix,[3] and $\Delta \dot{\mathbf{q}} = d\mathbf{q}/dt$ is the velocity vector in internal coordinates. Some complications in calculating the G matrix arise when the internal coordinates are specified using dummy atoms (see Appendix). The motion of this system can be determined from the Lagrangian equation:

$$\frac{d}{dt} \frac{\delta T}{\delta \Delta \dot{\mathbf{q}}} + \frac{\delta E(\mathbf{q})}{\delta \Delta \mathbf{q}} = 0 \qquad (3)$$

Insertion of eqs 1 and 2 into (3) and truncating to second order yields

$$\mathbf{G}^{-1} \Delta \ddot{\mathbf{q}} + \mathbf{g} + \mathbf{H}_q \Delta \mathbf{q} = 0 \qquad (4)$$

where $\Delta \ddot{\mathbf{q}} = d\Delta \dot{\mathbf{q}}/dt$ is the acceleration vector. Multiplying the left-hand side of eq 4 by G and rearranging gives the following expression for the acceleration vector:

$$\Delta \ddot{\mathbf{q}} = -(\mathbf{G}\mathbf{g} + \mathbf{G}\mathbf{H}_q \Delta \mathbf{q}) \qquad (5)$$

For $\mathbf{q} = \mathbf{q}'$, a point on the reaction path, the acceleration vector and hence the displacement along the reaction path can be written as

$$\Delta \ddot{\mathbf{q}} = -\mathbf{G}\mathbf{g} \qquad (6)$$

The reaction path can then be expressed as

$$\frac{d\mathbf{q}(s)}{ds} = -N\mathbf{G}\mathbf{g} \qquad (7)$$

where N is a suitable normalization factor (see below). This gradient equation is the internal coordinate equivalent of the IRC of Fukui. The same expression has been obtained by Quapp and Heidrich[4] by applying a coordinate transformation to the steepest descent path in mass-weighted Cartesians.

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(2) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989,** *90,* 2154.
(3) Wilson, E. B.; Decius, G. C.; Cross, P. C. *Molecular Vibration;* McGraw-Hill: London, 1955.
(4) Quapp, W.; Heidrich, Dietmar. *Theor. Chim. Acta* **1984,** *66,* 245. Sana, M.; Reckinger, G.; Leroy, G. *Theor. Chim. Acta* **1981,** *58,* 145.

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