The Stabilities of α-Oxy and α-Thio Carbenium Ions: the Importance of the Ground-state Energies of the Neutral Precursors

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The abilities of oxy and thio substituents to stabilize an adjacent carbenium ion centre have been evaluated by *ab initio* methods, up to the MP3/6-31G* level of theory. The relative stabilities of $RXCH_2^+$ (X = O or S; R = H or CH_3) have been calculated by using the hydride-transfer equation $ROCH_2^+ + CH_3SR \longrightarrow CH_3OR + RSCH_2^+$. $HOCH_2^+$ is calculated to be more stable than $HSCH_2^+$ by 2.3 kcal mol^{-1}, and $CH_3SCH_2^+$ is more stable than $CH_3OCH_2^+$ by 0.7 kcal mol^{-1}. On the other hand, when chlorides are used as the precursors, the equation $ROCH_2^+ + RSCH_2Cl \longrightarrow RSCH_2^+ + ROCH_2Cl$ is exothermic, *e.g.* by 2.9 kcal mol^{-1} for R = H (MP3/6-31G*) and *ca.* 2—3 kcal mol^{-1} (estimated for MP3/6-31G*) for R = CH_3. The latter value is in excellent agreement with recent ion cyclotron resonance experiments. The apparent contrast between the conclusions from the foregoing equations regarding the relative stabilities of $RSCH_2^+$ and $ROCH_2^+$ results from significant ground-state stabilization of $ROCH_2Cl$ relatively to $RSCH_2Cl$. The energies of the two isodesmic equations show a strong dependence on the basis set, and reliable results are obtained only when both *d*-functions and correlation energy are included in the calculations. The possible correlation of the π-donation abilities and other charge-related criteria of the RS and RO substituents with the stabilities of $RSCH_2^+$ and $ROCH_2^+$ is analysed and critically discussed. It is concluded that such correlations should be treated with great caution, in particular when first- and second-row substituents are compared.

The ability of α-oxy and α-thio substituents to stabilize charged reactive intermediates has been the subject of numerous studies.[1—14] It is well established that carbanions are generally better stabilized by second-row substituents, including SR, than by the corresponding first-row substituents, including OR.[1] On the other hand evidence regarding the analogous α-SR and α-OR substituted carbenium ions is still inconclusive, despite numerous experimental (both gas-phase[2—6] and in solution[13,14]) and theoretical[7—12] studies.

In 1965 Taft, Martin, and Lampe studied the appearance potentials of the cations CH_2XR^+ (X = O or S; R = H or CH_3) and concluded that, relative to the corresponding hydrocarbons, SH and SCH_3 are 4 and 5 kcal mol^{-1}† more stabilizing than OH and OCH_3, respectively.[2] Field and Weeks found by chemical ionization techniques that $CH_3SCH_2^+$ is produced from methylthiomethyl acetate (or propionate) more readily than $CH_3OCH_2^+$ is generated from $CH_3CO_2CH_2OCH_3$.[3] While this may suggest that $CH_3SCH_2^+$ is more stable than $CH_3OCH_2^+$, the authors point out that different fragmentation mechanisms or differences in the ground-state energies of the two reactants may also be responsible for these results.[3] Keyes and Harrison compared the intensities of the major ions containing sulphur or oxygen in the mass spectra of CD_3XH, C_2D_5XH, CH_3XCD_3, and $C_2H_5XCD_3$, where X = S or O.[4] For the molecular ions they found that the sulphur-containing ions have the higher intensities, but for the ions CD_2XR^+ (R = H or CH_3) the opposite was observed: the intensity of the CD_2SR^+ peak was lower than that of the corresponding CD_2OR^+ peak. It was concluded that, relative to the parent molecular ions, the stability of the ions $ROCH_2^+$ is higher by 30—40 kcal mol^{-1} than that of the corresponding ions $RSCH_2^+$.[4] In a subsequent study, Harrison, Finney, and Sherk measured the abundance of the ions CH_2XH^+ (X = O or S), which are generated from a common precursor $HOCH_2CH_2SH$ *via* two competing fragmentations [equation (1)].[5] At low electron energies (10—15 eV) the $[HOCH_2^+]/[HSCH_2^+]$ abundance ratio is approximately 1, suggesting that the two ions have comparable stabilities.[5] The apparent discrepancy in the conclusions of the two related fragmentation experiments[4,5] results, as Harrison *et al.* have pointed out,[5] from the use of different precursors in these two experiments. This point is discussed in more detail later.

$$HOCH_2CH_2SH \longrightarrow [HOCH_2CH_2SH]^{+\cdot} \begin{cases} \longrightarrow HOCH_2^+ + CH_2SH^{\cdot} \\ \longrightarrow HSCH_2^+ + CH_2OH^{\cdot} \end{cases} \qquad (1)$$

More recently, Pau, Ruggera, Kim, and Caserio used ion cyclotron resonance techniques to measure the equilibrium constants for the chloride-transfer reactions between the methoxy- and mercapto-substituted ions [equation (2b)],[6a] and concluded that (relative to the neutral chlorides) $CH_3SCH_2^+$ is more stable than $CH_3OCH_2^+$ by more than 2.4 kcal mol^{-1}.[6b]

$$ROCH_2^+ + ClCH_2SR \longrightarrow ROCH_2Cl + RSCH_2^+ \qquad (2)$$
$$a;\ R = H \qquad b;\ R = CH_3$$

To summarize, the literature on the relative stabilities of $RSCH_2^+$ and $ROCH_2^+$ in the gas phase is inconclusive and complicated by the choice of different precursors and reference compounds.

Studies of this problem in the condensed phase have not reached a consensus either.[13] For example, the σ_p^+ values of the CH_3O and CH_3S groups (−0.778 and −0.604, respectively[13a]) indicate that a methoxy substituent stabilizes the cumyl cation more effectively than does the methylthio group. Similarly, Modena *et al.*[13b] found that $ClCH_2OCH_3$ is solvolysed *ca.* 110 times faster than $ClCH_2SCH_3$ in dioxane–water mixtures (under these conditions both compounds are believed to undergo solvolysis by an S_N1 mechanism).[13b,c] On the other

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† 1 kcal = 4.184 kJ.

Table 1. Total energies[a] at various theoretical levels and zero point energies (ZPE) at 3-21G for $RXCH_2^+$, $RXCH_3$, and $RXCH_2Cl$ (R = H or CH_3; X = O or S)[g]

	Basis set							
Compound	3-21G	3-21G*	3-21G*[h]	6-31G[i]	6-31G*	MP2/6-31G*[b]	MP3/6-31G*[b]	ZPE[c]
X = O								
$HOCH_2^+$	−113.514 14	−113.597 25	−113.600 17[d]	−114.096 22	−114.154 36	−114.442 61	−114.453 11	26.71
$CH_3OCH_2^+$	−152.349 34			−153.125 63	−153.200 44	−153.616 43	−153.635 37	45.62
$HOCH_3$	−114.398 02	−114.464 81	−114.466 25[d]	−114.987 60	−115.033 78	−115.345 38	−115.360 98	34.19
CH_3OCH_3	−153.213 12				−154.062 31	−154.501 97	−154.526 44	53.70
$HOCH_2Cl$	−571.121 30				−573.937 69	−574.386 20	−574.407 52	28.71
CH_3OCH_2Cl	−609.935 09			−612.878 13	−612.965 46			48.02
X = S								
$HSCH_2^+$[e]	−434.609 19	−434.777 59	−434.779 88	−436.735 13	−436.805 09	−437.055 94	−437.075 81	23.01
$CH_3SCH_2^+$	−473.453 91			−475.777 81	−475.857 35	−476.241 57	−476.272 51	42.86
$HSCH_3$[f]	−435.526 29	−435.668 54	−435.671 19	−437.647 53	−437.697 90	−437.960 66	−437.987 56	30.57
CH_3SCH_3	−474.348 44				−476.730 96	−477.126 95	−477.162 40	50.95
$HSCH_2Cl$	−892.234 66				−896.590 92	−896.992 62	−897.025 40	24.94
CH_3SCH_2Cl	−931.059 68			−935.541 98	−935.626 06			45.22

[a] In hartrees; using optimized 3-21G geometries. [b] In the MP2 and MP3 calculations for second-row elements only the 1*s* shell is kept frozen (in standard calculations the 1*s*, 2*s*, and 2*p* shells are kept frozen). [c] In kcal mol^{-1}. [d] At $3\text{-}21G^{(*)}(O)//3\text{-}21G^{(*)}(O)$ (*d*-orbitals augmented only oxygen) the total energies for CH_2OH^+ and CH_3OH are: −113.559 51 and −114.430 63 hartrees, respectively. [e] The energies at $3\text{-}21G^{(*)}//3\text{-}21G^{(*)}$ and $3\text{-}21G^{(*)}//3\text{-}21G$ are −434.743 74 and −434.741 25 hartrees, respectively. [f] At $3\text{-}21G^{(*)}//3\text{-}21G^{(*)}$ and $3\text{-}21G^{(*)}//3\text{-}21G$ the energies are −435.637 28 and −435.635 25 hartrees, respectively. [g] The energies of $RXCH_2^+$ (X = O or S), up to MP2/6-31G*, were reported in ref. 16*a*. [h] Using 3-21G* optimized geometries. [i] At MP2/6-31G the total energies for $CH_3OCH_2^+$, CH_3OCH_2Cl, $CH_3SCH_2^+$, and CH_3SCH_2Cl are: −153.418 56, −613.227 49, −476.020 48, and −935.831 23 hartrees, respectively.

hand, in 0.5—3.0M-H_2SO_4 the hydrolysis rate ratios (k_O/k_S) of dimethoxymethane and methoxymethylthiomethane are 0.12—0.08 (depending on the acid concentration).[13b] Examination of other reactions leading to α-thio or α-oxy carbenium ions shows that the k_O/k_S values range from *ca.* 0.1 to 440.[13b–f] The apparent inconsistencies amongst the various experiments in solution is not unexpected, because in addition to the ion stabilities other factors, such as solvation and the structure of the transition state (*e.g.* 'early' or 'late'), are involved. Thus, the foregoing studies do not provide a direct measure of the relative stabilities of the ions in question (this conclusion has been stated by others; for further discussion see ref. 13*b*).

We have applied *ab initio* molecular orbital calculations to this problem, in an attempt to resolve the conflicting data regarding the abilities of α-oxy and α-thio substituents to stabilize carbenium ions. We have also analysed in some detail the mechanisms by which these substituents interact with the adjacent positive centre. In particular, we have addressed the question as to whether the abilities of these substituents to disperse the positive charge by resonance parallel their thermodynamic stabilities, as is often assumed.[15]* Previous theoretical studies[7–12] of $RSCH_2^+$ and $ROCH_2^+$ have mostly concentrated on qualitative aspects but have not reached a definite quantitative conclusion regarding their relative stabilities. After the completion of this study Bernardi *et al.*[16a] published a closely related computational paper, and at a recent meeting Schleyer[16b,c] addressed some aspects of SH and OH substituent effects. The findings of the previous theoretical contributions are compared with ours in the present paper.

Method

The calculations used standard *ab initio* SCF-MO methods and were carried out by using the Gaussian 80[17a] and the Gaussian 82[17b] series of programs. The geometries of all molecules were fully optimized by using the split-valence 3-21G[18] basis-set and gradient-minimization techniques.[19] Some of the smaller species were also optimized with the $3\text{-}21G^{(*)}$ (including six *d*-functions on S and Cl),[20a] the 3-21G* (including six *d*-functions on all non-hydrogen atoms),† and the 6-31G*[21] basis sets (standard exponents[20,21] were used throughout). Single-point 6-31G* calculations at the best available geometries were also carried out. Electron correlation energies were evaluated by using Møller–Plesset perturbation theory[22] up to third order (denoted as MP3/6-31G*//3-21G for a single-point MP3/6-31G* calculation at the optimized 3-21G geometry). Zero point energies (ZPE) were calculated with the 3-21G basis set. The total energies of all species are presented in Table 1 and the optimized geometries are given in Figure 1.

Results and Discussion

Stabilization of Carbenium Ions by α-OR *and* α-SR *Substituents.*—The stabilities of the ions CH_2XR^+ (X = O or S; R = H or CH_3) relative to the parent methyl cation are given by the isodesmic[23] equations (3) for X = O and (4) for X = S.

$$CH_3^+ + CH_3XR \longrightarrow CH_4 + RXCH_2^+$$

$$X = O\text{: a; } R = H \quad \text{b; } R = CH_3$$
$$\text{c; } R = H\text{, RXCH angle in } RXCH_2^+ = 90^\circ \qquad (3)$$

$$X = S\text{: a; } R = H \quad \text{b; } R = CH_3$$
$$\text{c; } R = H\text{, RXCH angle in } RXCH_2^+ = 90^\circ \qquad (4)$$

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* A referee pointed out that as we use MO theory to perform the calculations it is not valid, from a strict theoretical viewpoint, to analyse our results using the language of valence bond theory. However, we have chosen to do precisely that, following the common practice of most papers in organic chemistry. We believe that the omission from the discussion of 'illegal' terms such as 'lone pairs' or 'resonance structures' will make the paper more difficult and less attractive to read to most organic chemists, who still use extensively valence bond terms and language.

† This is not one of Pople's 'standard' basis sets. A set of *d* orbitals augmented all first- and second-row atoms, following the guidelines used for constructing 3-21G(*). This basis set was used recently by S. M. Bachrach and A. J. Streitwieser (*J. Am. Chem. Soc.*, 1985, **107**, 1186).

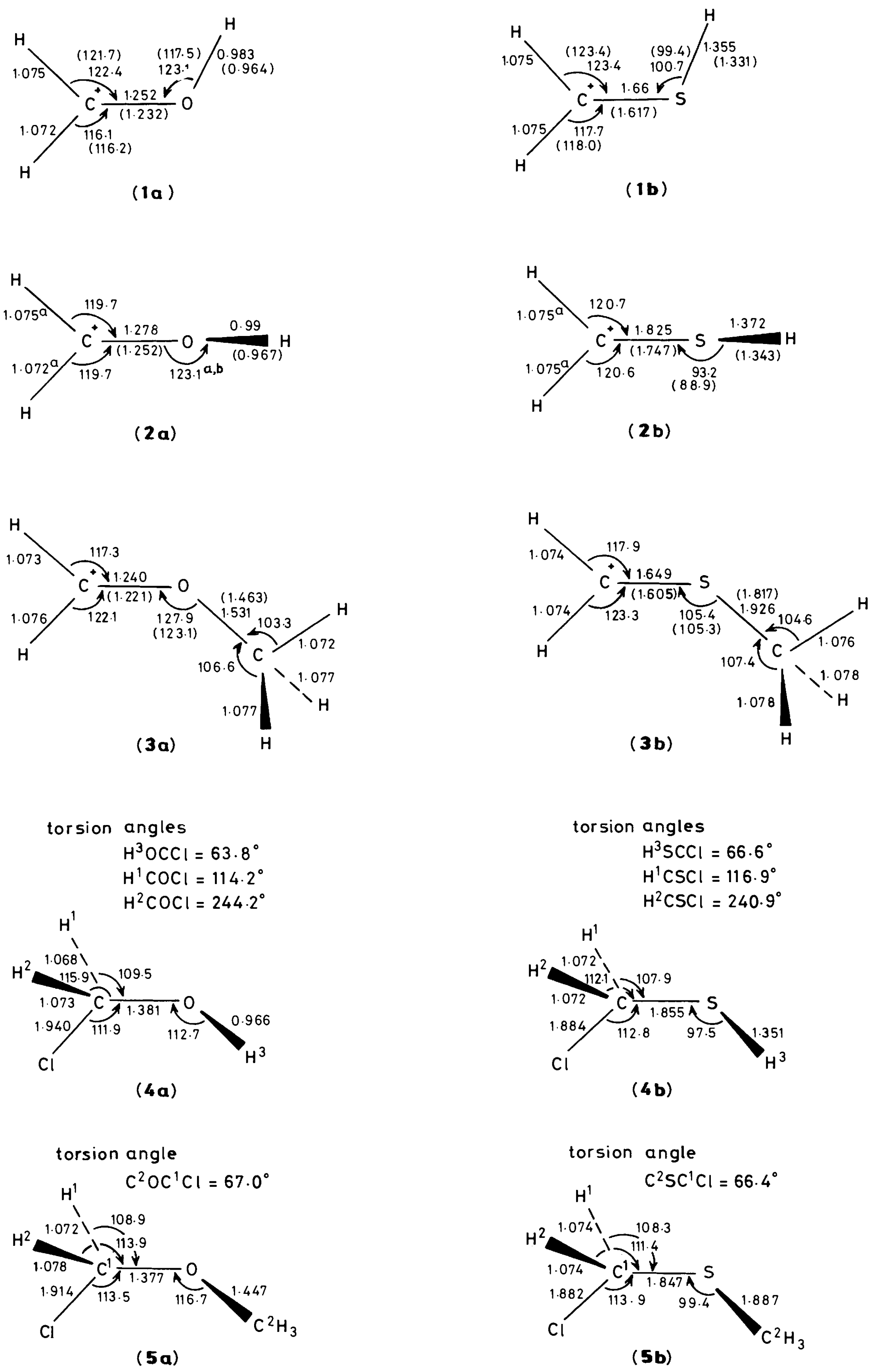


Figure 1. 3-21G-Optimized geometries of CH_2XR^+ and $ClCH_2XR$ (X = O or S; R = H or CH_3); values in parentheses are optimized at 6-31G* (the other parameters were kept at the 3-21G values); (a) this value taken from the appropriate planar conformer is kept constant; (b) upon optimization the HOC angle opens to 180° [35d]

Table 2. Stabilization energies[a] calculated for isodesmic equations (2)—(7) at various theoretical levels[b,c]

	Basis set				
Eqn.	3-21G	6-31G*	MP2/6-31G*	MP3/6-31G*	Experimental
(2a)	11.5 (11.6)	1.6 (1.7)	−4.3 (−4.2)	−3.0 (−2.9)	
(2b)	12.6	2.3	−3.9[d]		
(3a)	−52.6 (−50.9) −61.5,[h] −60.6[j]	−53.4 (−51.7) −45.8[i]	−65.6[e] (−63.6)	−62.1 (−60.4)	−65.5,[f] −60.0[g]
(3b)	−65.2 (−64.1)	−64.4 (−63.3)	−76.4 (−75.3)	−72.7 (−71.6)	−78.0,[f] −69.0[g]
(4a)	−31.8 (−30.2) −46.7,[h] −46.6[k]	−45.0 (−43.4) −32.6[i]	−64.4 (−62.8)	−59.7 (−58.1)	−64.0[g]
(4b)	−45.9	−57.8	−76.5	−73.4	−74.0[g]
(5a)	20.8 (20.7) 14.8,[h] 6.0,[k] 14.0[j]	8.4 (8.3) 9.3,[m] 13.2[i]	1.2 (1.1)	2.4 (2.3)	1.5[l]
(5b)	19.3[n]	7.4[n]	−0.1[n]	−0.7[n]	
(6a)	6.7	6.7	8.4	7.3	
(6b)	−2.7	−0.1	2.9	1.8	
(7a)	−9.4 (−9.3)	−6.8[o] (−6.7)	−5.5 (−5.4)	−5.5 (−5.4)	

[a] In kcal mol^{-1}. [b] Values in parentheses include zero point energies (ZPE). [c] The geometries were optimized at 3-21G. [d] Calculated using the 'additivity equation' developed by Radom.[25b] [e] The inclusion of ZPE increases the reaction energy, in contrast to the statement of Schleyer (ref. 16*c*, Table 1, footnote *i*). [f] Ref. 35*a*. [g] Ref. 2. [h] At 3-21G*//3-21G*. [i] At 6-31G. [j] *d*-Orbitals augmented only oxygen and second-row elements, denoted in the text as $3\text{-}21G^{(*)}(O)$. [k] At $3\text{-}21G^{(*)}//3\text{-}21G^{(*)}$. [l] Ref. 26. [m] At 6-31G*//6-31G*. [n] Addition of ZPE contributes less than 0.01 kcal mol^{-1}. [o] Stabilization energy for equation (7b) is −5.1 kcal mol^{-1}.

A direct comparison of the oxygen- and the sulphur-substituted cations is given by the hydride-transfer equations (5a) for R = H and (5b) for R = CH_3. Equations (5a and b) are obtained by subtracting equations (3) from (4). The calculated energies of equations (2)—(5) are presented in Table 2.

$$CH_2OR^+ + CH_3SR \longrightarrow CH_3OR + CH_2SR^+ \quad (5)$$
$$\text{a; } R = H \qquad \text{b; } R = CH_3$$

Table 2 reveals that the calculated relative stabilities of $ROCH_2^+$ and $RSCH_2^+$ [equation (5)] are strongly dependent on the basis set. At 3-21G the α-oxy cations are substantially more stable than the thio analogues [*i.e.* ΔE(5a) = 20.8 kcal mol^{-1}, ΔE(5b) = 19.3 kcal mol^{-1}].[24] Addition of polarization functions reduces these energy differences, and at 6-31G*//3-21G CH_2OH^+ and $CH_3OCH_2^+$ are more stable by only 8.4 and 7.4 kcal mol^{-1} than CH_2SH^+ and $CH_3SCH_2^+$, respectively. Geometry optimizations at 6-31G* have a small effect on these relative stabilities. At 6-31G*//6-31G* ΔE(5a) = 9.3 kcal mol^{-1}. The higher stabilities of the α-oxy cations vanish when electron correlation is included. At MP2/6-31G*//3-21G the stabilities of the thio and oxy cations are nearly equal [*i.e.* ΔE(5a) = 1.2 kcal mol^{-1}, ΔE(5b) = −0.1 kcal mol^{-1}]. Our best theoretical estimate of ΔE(5a), which used the MP3/6-31G*//3-21G energies and the 3-21G ZPE,[25a] is 2.3 kcal mol^{-1}. Similarly, for the methyl-substituted cations our best estimate (Table 2) is ΔE(5b) = −0.7 kcal mol^{-1}. Very similar results were published recently by Bernardi *et al.*,[16a] and by Schleyer, who has reported the most elaborate calculation (MP4SDTQ/6-31G*//6-31G*) for ΔE(5a) of 1.3 kcal mol^{-1}.[16b,c]

Thus, according to the calculations, in the gas phase, OH substitution is more stabilizing by 1.3 kcal mol^{-1} than SH substitution, while SCH_3 and OCH_3 stabilize the cation almost to the same degree. These results are in excellent agreement with the mass spectroscopic measurements of Taft *et al.*,[2] and those of Harrison, Finney, and Sherk.[5] The theoretical results can account also for the earlier puzzling experiments of Keyes and Harrison (see before), that showed that, relative to the molecular ions $RXCH_3^{+\cdot}$ (X = O or S; R = H or CH_3), the cations $ROCH_2^+$ are substantially more stable than the corresponding cations $RSCH_2^+$.[4] As Keyes and Harrison noted, these results reflect, in addition to the stabilities of the fragment cations, the relative energies of the molecular ions. Using Keyes and Harrison's data for the cations[4] and the known heats of formation of CH_3OH and CH_3SH[26] we calculate that ΔE(5a) = 1.5 kcal mol^{-1}, in excellent agreement with the other calculations. A reinterpretation of Harrison's experiments[4,5] using this information leads to the interesting conclusion that the higher ionization potential (by 30 kcal mol^{-1}) of CH_3OR than of CH_3SR[27] is fully compensated by the lower dissociation energy of the C–H bond α to oxygen relatively to that α to sulphur.

The most accurate experimental determination of the relative stabilities of $CH_3SCH_2^+$ *vs.* $CH_3OCH_2^+$ is probably given by the ion cyclotron resonance (ICR) measurements.[6a] Pau *et al.* ionized in a trapped ICR cell a mixture of $ClCH_2OCH_3$ and $ClCH_2SCH_3$, and followed the rapid decay of the initially formed $CH_3OCH_2^+$ fragments and the simultaneous build-up of $CH_3SCH_2^+$ ions, according to equation (2b). The equilibrium of equation (2b) lies strongly to the right, and it was not possible to determine the equilibrium constant accurately. Pau *et al.* concluded that with respect to chloride transfer, *the thio cation is more stable than the corresponding oxy cation* and estimated that ΔG(2b) is exothermic by more than 2.4 kcal mol^{-1}.[6b]

Do the calculations reproduce the ICR value? The best calculated energy of equation (2a) is −2.9 kcal mol^{-1} (MP3/6-316*//3-21G + ZPE). To model more closely the ICR experiment [equation (2b)], we studied the effect of methyl substitution at the heteroatom. Owing to computational limitations we can calculate ΔE(2b) only up to the 6-31G* level. At this level, relative to the corresponding chlorides, $CH_3SCH_2^+$ is less stable by 2.3 kcal mol^{-1} than $CH_3OCH_2^+$. Using Radom's 'additivity procedure' for estimating the effect of electron correlation {*i.e.* ΔE[MP2/6-31G*(est.)] = ΔE(MP2/6-31G) + ΔE(HF/6-31G*) − ΔE(HF/6-31G)[25b]}, we find that the relative stabilities of the cations are reversed. At MP2/6-31G*(est.), $CH_3SCH_2^+$ is more stable by 3.9 kcal mol^{-1} than $CH_3OCH_2^+$, relative to the corresponding chlorides. Explicit MP2/6-31G* calculations for equation (2a) (see before) show a similar effect of electron correlation. As MP2 usually overestimates the effect of electron correlation,[23b,25b] we expect that at higher orders of Møller–Plesset theory ΔE(2b) would actually be less exothermic by 1—2 kcal mol^{-1}. This correction puts the calculated ΔE(2b) at -2 to -3 kcal mol^{-1}, in excellent agreement with the experimental estimate of Pau *et al.*[6a] This agreement increases our confidence in the ability of these theoretical methods to describe correctly the energies of the molecules of interest here, and in the analysis that follows.

Note that, at first glance, the ICR results appear to conflict with the foregoing theoretical estimate [*cf.* equation (5)], as well as with earlier gas-phase measurements.[2,5] Pau *et al.* hinted that this may result from the fact that equation (2) includes both the cations and the corresponding precursor chlorides.[6a] However, as the heats of formation of the chlorides were (and still are) unknown it was not possible to evaluate their contribution to the equilibrium constant of equation (2b). Thus, the 'inherent' relative stability of $CH_2SCH_3^+$ *vs.* $CH_2OCH_3^+$, *i.e.* with respect to hydride transfer [equation (5b)], could not be determined from the experiments of Pau *et al.* We analyse this point later.

Ground-state Energies of $ClCH_2SR$ *and* $ClCH_2OR$.—The separation of ground-state effects from the 'inherent' cation stabilities, which is not available from experimental results in this case,[6a] is easily accomplished by theory. Equations (3) and (4) measure the 'inherent' stabilities of the cations (relative to the corresponding hydrocarbons) and equations (6a and b) measure the interactions in the neutral precursors, between chlorine and OH or SH, respectively.

$$ClCH_2XH + CH_4 \longrightarrow CH_3Cl + CH_3XH \qquad (6)$$
$$\text{a; } X = O \qquad \text{b; } X = S$$

$$CH_3OR + ClCH_2SR \longrightarrow CH_3SR + ClCH_2OR \qquad (7)$$
$$\text{a; } R = H \qquad \text{b; } R = CH_3$$

How large are the ground-state interactions in $ClCH_2OH$ and $ClCH_2SH$? The bond-separation energy of $ClCH_2OH$ is 7.3 kcal mol^{-1} [equation (6a), MP3/6-31G*//3-21G], indicating significant stabilization of the geminally substituted molecule relative to CH_3Cl and CH_3OH. The interaction in $ClCH_2SH$ is much smaller, only 1.8 kcal mol^{-1}. Thus, the stabilizing geminal interactions in $ClCH_2OH$ are larger than in $ClCH_2SH$ by 5.5 kcal mol^{-1} [equation (7a)]. The higher stability of $ClCH_2OH$ than of $ClCH_2SH$ was noted recently also by Schleyer and his co-workers.[16b,c,28a]

Let us discuss in some more detail the electronic interactions in the $ClCH_2XH$ precursors, by using two approaches: (*a*) PMO theory and (*b*) analysis of the barriers to rotation around the C–X bonds in $ClCH_2SR$ and $ClCH_2OR$.

(a) PMO *analysis.* The geminal interactions between the substituents in XCH_2Y[28a–c] are commonly referred to as the 'anomeric' effect.[29] In MO terms the 'anomeric' effect is analysed as resulting from interactions between lone pair electrons on X and the σ and σ^* orbitals of the geminal C–Y bond [owing to their symmetry σ and σ^* are more appropriately denoted as $\pi(CH_2–Y)$ and $\pi^*(CH_2–Y)$]. In $ClCH_2XH$ (X = O or S) two pairs of such interactions are involved: one between the lone pairs of X (denoted *p*) and the C–Cl bond, and the second between the lone pairs on chlorine and the C–X bond. In each case the p–σ interactions involve four electrons and are thus destabilizing, while the p–σ^* interactions involve two electrons and are stabilizing.[30,31] The interaction with σ^*(C–Y) is believed to be dominant.[29–31] A schematic hyperconjugative interaction diagram for $ClCH_2OH$ and $ClCH_2SH$ is presented in Figure 2. The orbital energies in Figure 2, which are based on 3-21G//3-21G calculations on model systems such as CH_3OH, CH_3SH, and CH_3Cl, are generally in good agreement with available experimental values.[27] According to PMO theory the interaction (ΔE)

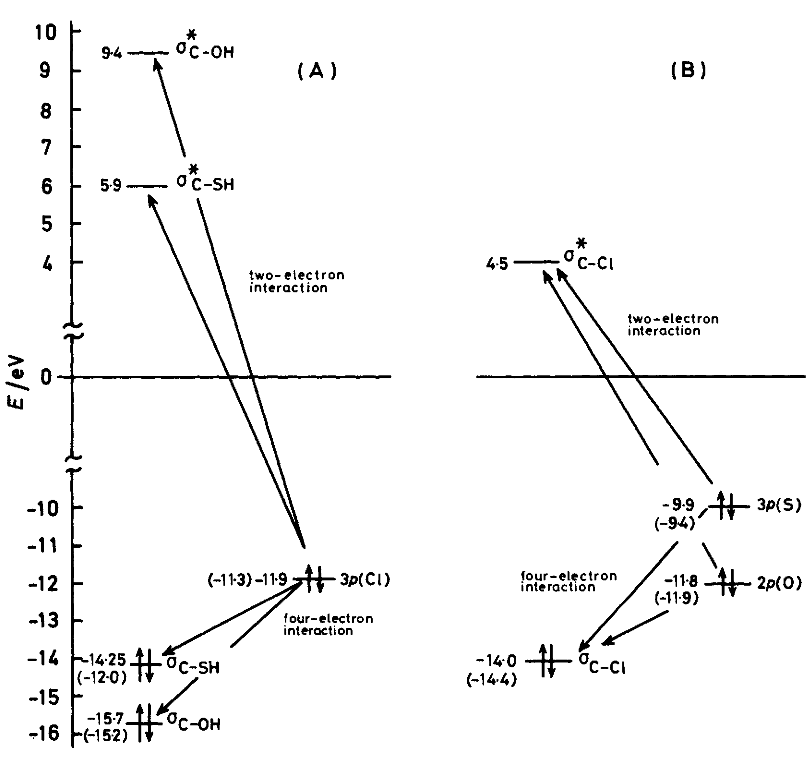


Figure 2. A schematic orbital interaction diagram for $HXCH_2Cl$ (X = O or S); orbital energies (in eV) were obtained from 3-21G calculations on CH_3OH, CH_3SH, and CH_3Cl; experimental values[27] in parentheses

Table 3. Total energies[a] at various torsion angles, θ[b] rotation barriers $V_T(\theta)$, and the V_1, V_2, and V_3 terms of equation (9) (kcal mol^{-1})

Compound	θ	E[a]	$V_T(\theta)$	V_1	V_2	V_3
$HOCH_2Cl$	63.8[c]	−573.937 69	−3.49	5.62	−4.66	−1.35
	0.0	−573.932 13	0.0			
	90.0	−573.936 15	−2.52			
	180.0	−573.925 33	4.27			
$HSCH_2Cl$	66.6[c]	−896.590 92	−3.04	1.76	−2.40	−1.60
	0.0	−896.586 06	0.0			
	90.0	−896.590 01	−2.48			
	180.0	−896.585 81	0.16			
CH_3OCH_2Cl	67.0[c]	−612.965 46	−8.8 (−6.7)[d]	1.94	−6.96	−3.62
	0.0	−612.951 44	0.0 (0.0)[d]	−0.25[d]	−4.4[d]	−3.0[d]
	90.0	−612.963 86	−7.8 (−6.0)[d]			
	180.0	−612.954 11	−1.68 (−3.25)[d]			
CH_3SCH_2Cl	66.3[c]	−935.626 06	−7.55	−0.20	−4.76	−3.58
	0.0	−935.614 02	0.0			
	90.0	−935.624 62	−6.65			
	180.0	−935.620 04	−3.78			

[a] Calculated at 6-31G*, in hartrees; the geometries are obtained by rigid rotation of the 3-21G-optimized equilibrium structures. [b] The R–X–C–Cl (R = H or CH_3; X = O or S) torsion angle. [c] The torsion angle at equilibrium. [d] For non-rigid rotation (see text).

between two orbitals i and j, one vacant and one filled, is given by equation (8), where S_{ij} is the overlap integral between the

$$\Delta E = S_{ij}^2/(\varepsilon_i - \varepsilon_j) \qquad (8)$$

orbitals, and ε_i and ε_j are the corresponding orbital energies.[30] The magnitude of ΔE increases as the orbital gap $(\varepsilon_i - \varepsilon_j)$ decreases and as S_{ij} becomes larger. Four-electron interactions become more destabilizing as the average energy of the interacting orbitals rises (*i.e.* as $\varepsilon_i + \varepsilon_j$ becomes less negative).[30,31]

The orbital energies in Figure 2 suggest that sulphur is a better π-donor than oxygen and that σ^*(C–S) is a better acceptor orbital than σ^*(C–O). Thus, on the basis of the energy criterion alone, hyperconjugation in $HSCH_2Cl$ is expected to be stronger than in $HOCH_2Cl$. The bond-separation energies of equations (6a and b) show that this is not the case. Apparently, the more favourable orbital energy gap in $ClCH_2SH$ is overridden by a much smaller overlap integral for S relative to O. The smaller S_{ij} for S results mainly from the longer C–S bond [*i.e.* r(C–S) = 1.86 Å in $ClCH_2SH$, *cf.* r(C–O) = 1.38 Å in $ClCH_2OH$]. In addition, the orbital coefficient on C is smaller in σ^*(C–S) than in σ^*(C–O), owing to the higher electronegativity of oxygen.[30,31] The stronger four-electron destabilizing interaction [*i.e.* p–σ(C–X)] for X = S relative to X = O also contributes to the smaller interaction energy (ΔE) in $ClCH_2SH$ relative to $ClCH_2OH$.

(b) *Barriers to rotation around the* C–X *bonds in* $ClCH_2XR$ (X = O, S). Information on the stereoelectronic requirements of the geminal interactions can be obtained from the barriers to rotation around the C–X bonds in $ClCH_2XR$ (X = O or S; R = H or CH_3). We have therefore performed, for these molecules, 6-31G*//3-21G calculations using the 'rigid rotor' model, *i.e.* changing the rotation angle but keeping all other geometrical parameters at the values of the conformer of lowest energy. 'Rigid rotor' barriers are not expected to reproduce accurately the experimental barriers, but they can reproduce trends and serve as upper limits to the actual barriers to rotation. All four compounds $HOCH_2Cl$, $HSCH_2Cl$, CH_3OCH_2Cl, and CH_3SCH_2Cl are calculated to adopt a *gauche* conformation, in agreement with experiment, with the RXCCl torsion angle θ = 63.8°, 66.6°, 67.0°, and 66.3°, respectively (Table 3). Calculations were then performed using the 'rigid rotor' model for 3 additional conformers with θ of 0°, 90°, and 180° and the results are presented in Table 3.

In these compounds there are two possible paths for internal rotation around the C–X bonds: one which passes through the synperiplanar conformation (θ = 0°), and the other through the antiperiplanar conformation (θ = 180°). We find that in both $ClCH_2OH$ and $ClCH_2SH$, the lowest-energy path for internal rotation passes through the synperiplanar conformation and the barriers in the two systems are similar (3.5 and 3.0 kcal mol^{-1}, respectively).

Following Pople *et al.*[32a] we analyse the barrier to internal rotation [$V_T(\theta)$] by using a three-term truncated Fourier expansion, as given in equation (9). The terms V_1, V_2, and V_3 (Table 3) are usually taken as measures of the dipole–dipole, stereoelectronic, and eclipsing steric interactions, respectively. The individual terms of equation (9) and the energies V_T are also displayed graphically in Figure 3.

$$V_T(\theta) = 0.5V_1(1 - \cos\theta) + 0.5V_2(1 - \cos2\theta) + 0.5V_3(1 - \cos3\theta) \qquad (9)$$

This analysis shows that although the total barriers in $ClCH_2OH$ and $ClCH_2SH$ are similar, the term V_2 which is associated with the stereoelectronic interactions is more stabilizing by *ca.* 2.3 kcal mol^{-1} for $ClCH_2OH$ than for $HSCH_2Cl$ (Table 3). This result supports the conclusion of the PMO analysis (see before) that *the 'anomeric' effect is larger in* $HOCH_2Cl$ *than in* $ClCH_2SH$. The similarity of the overall V_T values in the two systems results from the opposing effects of the V_1 term, which in $ClCH_2OH$ is higher by *ca.* 3.9 kcal mol^{-1} than in $ClCH_2SH$. This is reasonable as V_1 is associated with dipole–dipole interactions which are expected to be larger for the more electronegative oxygen (*i.e.* in $ClCH_2OH$). The high positive V_1 values coupled with the small V_3 values dictate that the lowest-energy path for internal rotation passes through the synperiplanar conformation (θ = 0°) rather than the antiperiplanar conformation (θ = 180°). The V_3 values, which are associated with the steric interactions in the eclipsed conformation, are, as expected, nearly the same in $ClCH_2OH$ and $ClCH_2SH$.

In $ClCH_2OCH_3$ and $ClCH_2SCH_3$ the terms V_1, V_2, and V_3 are very different from those in $ClCH_2OH$ and $ClCH_2SH$, respectively (Table 3). Thus, V_1 is larger for X = O than for X = S in the methylated derivatives, but the difference between the terms is much smaller than in $ClCH_2XH$. The term V_2 is also larger in CH_3XCH_2Cl (X = S or O) than in the corresponding $HXCH_2Cl$ derivatives, but here the difference

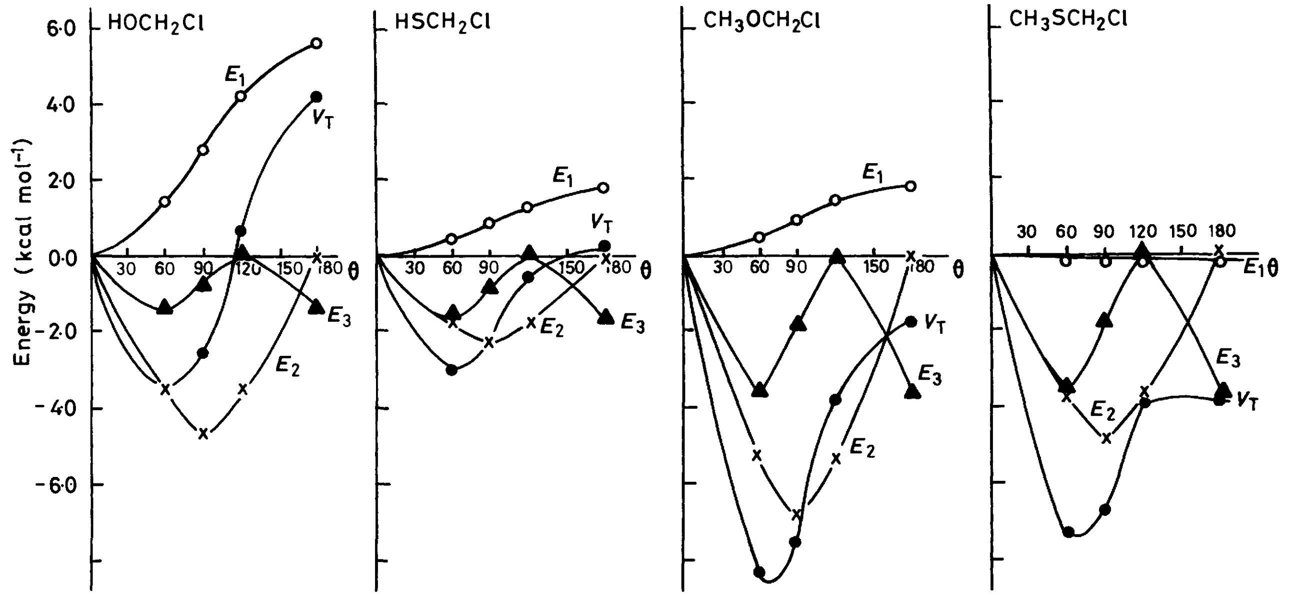


Figure 3. Fourier decomposition of the potential energy function as a function of the torsion angle θ(RXCCl) for $RXCH_2Cl$ (R = H or CH_3; X = S or O) according to equation (9); $V_T(\theta) = E_1(\theta) + E_2(\theta) + E_3(\theta)$; ○, $E_1 = 0.5V_1(1 - \cos\theta)$; ×, $E_2 = 0.5V_2(1 - \cos 2\theta)$; ▲, $E_3 = 0.5V_3(1 - \cos 3\theta)$. The 'rigid rotor' model (see text) and the 6-31G*//3-21G energies were used

between CH_3OCH_2Cl and CH_3SCH_2Cl is similar to that between $HOCH_2Cl$ and $HSCH_2Cl$ (*ca.* 2.2 kcal mol^{-1}). The increase in V_2 in the methyl-substituted compounds is due to the better donor properties of oxygen and sulphur when substituted with the electron-donating methyl group. The terms V_3 are practically the same in CH_3OCH_2Cl and CH_3SCH_2Cl and are also larger for CH_3XCH_2Cl than for $HXCH_2Cl$ (X = O or S), reflecting the higher steric requirements of methyl relative to hydrogen. In CH_3OCH_2Cl the sum of V_3 and V_1 is such that the antiperiplanar conformation is slightly favoured over the synperiplanar form [the contribution of V_2 is zero for both θ = 0° and θ = 180°; equation (9)]. Thus, in contrast to the parent $HXCH_2Cl$ where rotation occurs *via* the synperiplanar conformation, in CH_3OCH_2Cl and CH_3SCH_2Cl the lowest-energy path for internal rotation around the C–X bonds is *via* the antiperiplanar conformation. A previous theoretical study of CH_3OCH_2Cl by Jeffrey *et al.* (using the 4-31G basis set and standard geometries) reached similar conclusions, but their calculated barrier to rotation *via* the synperiplanar conformer is much larger (*ca.* 20 kcal mol^{-1})[32b] than ours (Table 3).

Anet and Yavari measured by n.m.r. techniques a barrier of 4.2 kcal mol^{-1} to internal rotation in CH_3OCH_2Cl, and attributed 2 kcal mol^{-1} to a steric barrier and *ca.* 2 kcal mol^{-1} to the anomeric effect.[32c] In agreement with Anet's suggestion we (as well as Jeffrey and Yates[32b]) find that the lowest rotation path involves the antiperiplanar conformation, the synperiplanar form being higher in energy. The calculated 'rigid' barrier to internal rotation is 7 kcal mol^{-1}, significantly higher than the experimental barrier.[32c] To check the reliability of the calculations we have optimized also the geometry of the antiperiplanar conformation of CH_3OCH_2Cl, and this reduces the barrier to 3.4 kcal mol^{-1}, in good agreement with the experimental measurements.[32c] Analysis of the barrier to rotation in CH_3OCH_2Cl according to equation (9) gives (in kcal mol^{-1}): $V_1 = -0.25$; $V_2 = -4.4$; $V_3 = -3.0$. According to this analysis, the major contribution to the barrier for internal rotation comes from hyperconjugation (V_2) and the steric barrier (V_3); the dipole–dipole interactions (V_1) have very small contribution (Figure 3). Jeffrey and Yates suggested that V_1 also plays an important role, but probably this is due to the restricted non-optimized geometries which they have used.

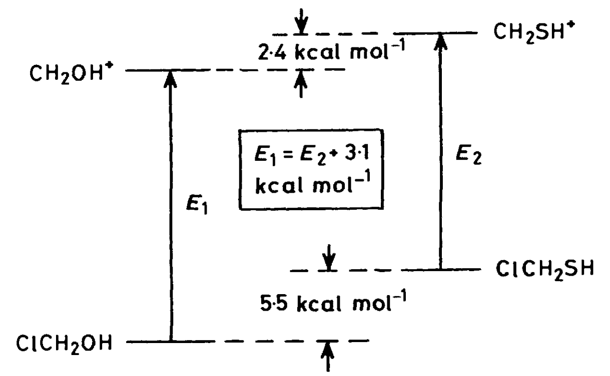
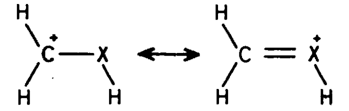


Figure 4. The relative gas-phase energies (MP3/6-31G*//3-21G) of the precursor chlorides $ClCH_2XH$ and the corresponding cations CH_2XH^+ (X = O or S). The relative energies of the thio and oxy systems are related by equations (5) (cations) and (7a) (neutrals)

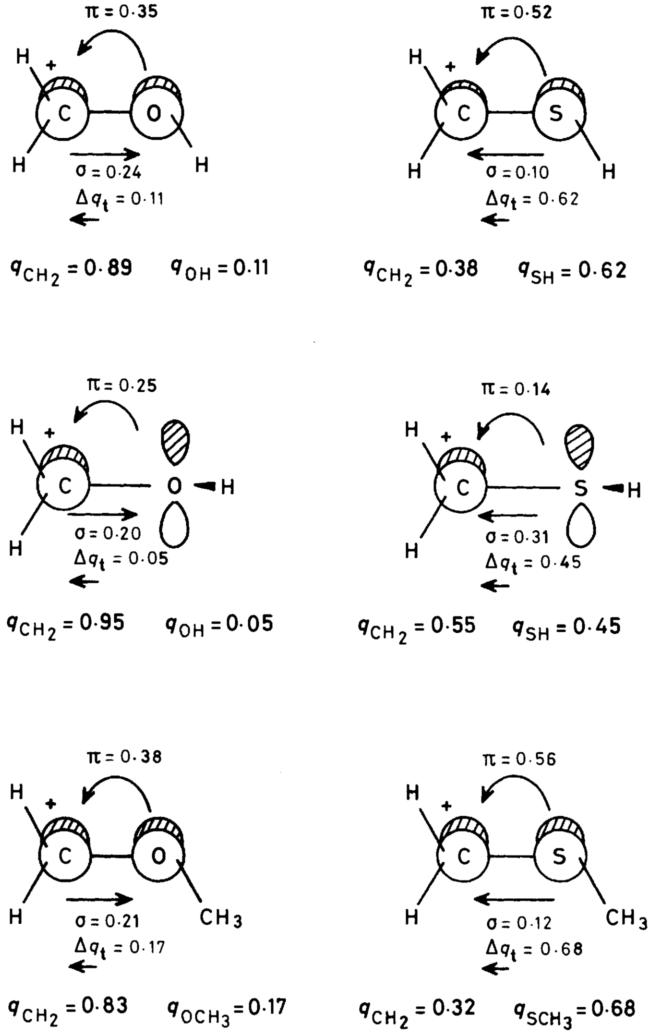
The Chlorine-transfer Reaction [*Equation* (2)].—Now that we have evaluated the relative stabilities of the neutral chlorides let us return to equation (2) (the experiment of Pau *et al.*[6a]). The foregoing analysis for the chlorides combined with the relative inherent stabilities of the cations [equation (5)] shows that the fact that the equilibrium of equation (2) lies strongly to the right [*i.e.* $\Delta E(2a) = -2.9$ kcal mol^{-1}, $\Delta E(2b) = -3.9$ kcal mol^{-1}] results mainly from the higher stability of $ROCH_2Cl$ relative to $RSCH_2Cl$, and not from a significantly higher stability of the thio-substituted cations. The relative energies of the precursors and of the cations are shown in Figure 4. We have reported on similarly significant ground-state effects also in the comparison of R_3SiCH_2OH and R_3CCH_2OH (R = H or CH_3).[33a–c] It appears that such *hyperconjugative ground-state effects are significant whenever first- and second-row substituents are compared*, and they are expected to play an important role both in the gas phase and in solution. In many studies, particularly solvolytic, these ground-state effects have been ignored and this may have led to erroneous interpretations regarding the relative stabilities of the ions involved. We hope that this paper will help to draw attention to this important factor.

To conclude, our calculations are in full harmony with the ICR results of Pau *et al.*, but in addition they provide insight into the factors that determine the position of the equilibrium of equation (2b). The foregoing analysis shows that *the fact that the equilibrium of equation* (2b) *lies strongly to the right is due mainly to the higher stability of* CH_3OCH_2Cl *relative to that of* CH_3SCH_2Cl, *and does not result from the higher stability of* $CH_3SCH_2^+$ *relative to* $CH_3OCH_2^+$. Relative to hydride transfer ('intrinsic' stability), these two cations are of nearly equal stability [equation (5b)]. Schleyer drew the same conclusions at a recent meeting.[16b]

The Stabilizing Mechanisms of the SR *and* OR *Substituents.*—Alkoxy and thio substituents stabilize an adjacent carbenium ion centre to a similar degree, but are the stabilization mechanisms for these substituents the same? We address this question later. We also examine the validity, in this specific case, of the widely used assumption that a correlation exists between the stability of a carbenium ion and the ability of the substituents to disperse (particularly by resonance) the positive charge.[15] It is 'common wisdom' that the stability of a cation increases as the substituent disperses the positive charge more effectively.[15a,b] In valence bond terms:* the stability of a carbenium ion increases when resonance hybrid (**6b**) contributes more to its structure.


(6a) **(6b)**

The stabilizing mechanisms of the SR and OR substituents have been discussed previously in some detail by Bernardi *et al.*[7,8] Yet we think that it is appropriate to add a few additional comments to these discussions. These authors analysed (on the basis of STO-3G and 4-31G calculations) the π-donation abilities and the stabilization energies of SR *vs.* OR substituents in several R–XH systems, where X = O or S and R = CH_2^+, CH_2=CH–, C_6H_5, or HC≡C–. Bernardi *et al.*[8] found computationally that the π-donation abilities and the stabilization energies of OR and SR substituents depend on the nature of R, and more specifically on the energy of its lowest unoccupied molecular orbital (LUMO). Thus, for R = CH_2=CH–, C_6H_5, or HC≡C–, which have relatively high LUMO energies, oxygen is a better π-donor than sulphur. However, when R is a good π-acceptor (*i.e.* low-energy LUMO) such as CH_2^+, sulphur becomes a better π-donor than oxygen. The suggestion of Bernardi *et al.* is supported by various experimental data some of which have been published only recently. Thus, a recent photoelectron and electron transmission study of C_6H_5XR showed that oxygen is a better π-donor than sulphur.[34] The foregoing conclusion for R = CH_2^+ is supported by the calculated barriers for rotation around the C–X bond in $HXCH_2^+$, which at 4-31G is larger for X = S (36.5 kcal mol^{-1})[7] than for X = O (23 kcal mol^{-1}; 25.9 kcal mol^{-1} at 6-31G*[35a]).[35c] The higher rotation barrier for X = S points to a higher C–X bond order in H_2CSH^+ than in H_2COH^+, suggesting a larger contribution of resonance structure (**6b**) in the former cation. However, this interpretation can be criticized on the grounds that the rotation barriers include a 'residual' resonance stabilization in the perpendicular structures (**2a**) and (**2b**), which are believed to be the transition states for the rotation (see later).[35a] This 'residual' resonance effect, resulting from interaction between $2p(C^+)$ and the 'sp^2-like' lone pair on X, might be different for X = O and X = S. Noe *et al.* found by dynamic n.m.r. techniques that the barriers to rotation around the carbonyl-X bond in R(C=O)XR′ are nearly the same for X = S and X = O (8.9 and 9.4 kcal mol^{-1}, respectively).[36] As H_2C^+ is a better π-acceptor than a carbonyl group, these results, coupled with the aforementioned study of C_6H_5XR,[34] point to a picture consistent with the conclusion that the relative π-donor abilities of S and O vary with the molecule in question and that in CH_2XH^+ sulphur is a better π-donor than oxygen.[8] Let us now turn to our analysis of this problem.



Scheme. 6-31G* σ- and π-charge transfers from X to CH_2^+ in CH_2XR^+ (X = O or S; R = H or CH_3)

(a) *The cations* CH_2OR^+ *and* CH_2SR^+. We will analyse the importance of resonance structures (**6a**) and (**6b**) on the basis of three criteria: (1) the calculated charge densities, derived from the Mulliken population analysis;[37] (2) the C–X bond lengths; and (3) the rotation barriers around the C–X bond in CH_2XH^+.

(1) *Charge densities.* In the Scheme we present the calculated

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* See footnote * on p. 626.

Table 4. π-Overlap integrals (S_{CX}),[a] bond lengths (R),[a,b] and barriers to rotation (ΔE_r)[a,b] around the C–X bond in CH_2XH^+

X	S_{CX}	ΔE_r[c]	R(C–X) in CH_2XH^+ (1)[d]	R(C–X) in CH_2=X[d]	R(C–X) in CH_3XH[d]	R(C–X) in CH_2XH^+ (2)[d]
S	0.2014	42.3	1.617	1.597	1.826	1.747
		(36.3)	(1.660)	(1.638)	(1.894)	(1.825)
O	0.2014	26.0[e]	1.232	1.184	1.399	1.252[e]
		(24.2)[e]	(1.252)	(1.207)	(1.440)	(1.278)[e]

[a] At 6-31G*. [b] Values in parentheses are at 3-21G. [c] In kcal mol^{-1}. [d] In Å. [e] The COH bond angle was kept at the optimized value of the planar conformation. Upon full geometry optimization this angle opens to 180°.[35d]

6-31G* total atomic charges† and the electron transfers, in the π- and σ-frameworks, between the XR and CH_2^+ units.‡ The data in the Scheme show that sulphur is a π- and a σ-electron donor, whereas oxygen is a π-donor but a σ-acceptor (the same qualitative trend was found at 4-31G[8,9]). With CH_2^+ as the acceptor group, sulphur is a significantly better π-donor than oxygen [the π-charge transfers are 0.52 and 0.35 electrons for SH and OH, respectively (Scheme)]. Sulphur also disperses the positive charge more effectively than oxygen. In CH_2SH^+ and $CH_2SCH_3^+$ nearly two-thirds of the unit positive charge resides on sulphur, whereas in CH_2OH^+ and $CH_2OCH_3^+$ most of the positive charge (*e.g.* 89% in CH_2OH^+ at 6-31G*) remains on the CH_2^+ fragment. Thus, the calculated charges suggest that the major contributing resonance structures are (**6a**) for $ROCH_2^+$, but (**6b**) for $RSCH_2^+$. This picture is in apparent conflict with Olah's suggestion, based on the ^{13}C n.m.r. chemical shifts for the cations R_2CXH^+, that the contribution of resonance structure (**6a**) is smaller for X = O than for X = S.[38a] However, this interpretation of the chemical shifts, which was based on the common assumptions that a decrease in bond order causes a decrease in the deshielding effect and that the changes in the chemical shifts as a functions of charge are the same for the protonated carbonyl and thiocarbonyl derivatives, may be complicated by various factors. Thus, Olah notes that calculated Hückel π-electron densities do not reproduce the ^{13}C chemical shifts in thioureas, and that in a series of protonated carbonyl compounds, the correlation line between the calculated π-electron charge densities and the ^{13}C chemical shifts has an unusually high slope of 306 p.p.m. per unit charge[38b] (*cf. ca.* 160 p.p.m. in most other systems[38c]). This may point to an unusual sensitivity of the ^{13}C resonances to the charge density in oxygenated cations.

The conclusion from the apparent disagreement between the calculated charge densities and the ^{13}C chemical shifts is that one cannot use the same correlation lines to compare protonated carbonyl and thiocarbonyl derivatives. Of course, we are not the first to point out that factors other than linear charge polarization can be extremely important in determining chemical shifts.[38c,d]

(2) *The* C–X *bond lengths.* In PMO language[30] the resonance stabilization (**6a**) $\longleftrightarrow$ (**6b**) is represented by a two-electron interaction between the vacant $2p(C^+)$ orbital and a lone pair on the heteroatom. The degree of stabilization (ΔE) increases as the overlap integral S between these orbitals increases and as their energy difference ($\Delta\varepsilon$) decreases [equation (8)]. The Mulliken π-overlap integrals (S) are nearly the same for X = S as for X = O (6-31G*). However, the sulphur $3p$-lone pair is higher in energy than the oxygen $2p$-lone pair (Figure 2) so that the energy gap ($\Delta\varepsilon$) to the $2p(C^+)$ orbital is smaller for sulphur.§ Thus, according to equation (8) the stabilizing interaction (ΔE) is larger in CH_2SH^+. The stronger resonance interaction in CH_2SH^+ than in CH_2OH^+ is reflected also in the corresponding C–X bond lengths. The C–X bond length (values at 6-31G*) in CH_2SH^+ is closer to that of a double bond [1.617 Å in (**1b**); 1.597 Å in H_2C=S] than in CH_2OH^+ [1.232 Å in (**1a**); 1.184 Å in H_2C=O]. Note that for both X = S and O the C–X bond length in (**1**) is closer to that of the double bond in the corresponding derivative CH_2=X than to the single bond in the corresponding CH_3XH (Table 3). Using these bond lengths we estimate¶ that the contributions of resonance structure (**6b**) to the structure of (**6**) are 91% for X = S and 78% for X = O.

(3) *The rotation barrier around the* C–X *bond.* The calculated barriers to rotation around the C–X bond in (**1**) support this trend. The rotation barrier is 42.3 kcal mol^{-1} in CH_2SH^+ and only 25.9 kcal mol^{-1} in CH_2OH^+ (6-31G*), pointing to a higher double-bond character in the former cation. As already mentioned, the rotation barriers reflect the difference in resonance stabilization in the planar conformers (**1**) and the corresponding perpendicular conformers (**2**), the latter being the highest energy points along the rotation co-ordinate. In CH_2SH^+ the degree of π-donation to the $2p(C^+)$ orbital is reduced considerably upon rotation, from 0.52 electrons in the planar conformer (**1b**) to 0.14 electrons in the perpendicular conformer (**2b**) (Scheme; 6-31G*). In contrast, in CH_2OH^+ the effect of rotation on the degree of charge transfer is much smaller. There is significant π-charge transfer to the cationic centre also in the perpendicular conformation [0.25 electrons in (**2a**); *cf.* 0.35 electrons in (**1a**)], pointing to strong conjugation in both conformations. This conclusion is supported by calculations[39] and analysis of the i.r. intensities of phenol and anisole[40] which reveal significant π-conjugation between the oxygen and the aromatic ring, in the perpendicular conformation also. The different degree of π-conjugation in the perpendicular conformations of the two cations is reflected in the stabilization which is provided by the substituents in (**2a**) and (**2b**) [equations (3c) and (4c)]. Thus, OH provides strong stabilization, *i.e.* 28 kcal mol^{-1} relative to hydrogen, even in the perpendicular conformation, while SH stabilizes (**2b**) by only 2.2 kcal mol^{-1} (6-31G*//6-31G*). Recall that in the planar structures (**1**) the corresponding stabilization energies are 53.7 and 44.5 kcal mol^{-1} (6-31G*//6-31G*) in CH_2OH^+ and

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† The contribution of d-orbitals to the total atomic charge densities of C, O, and S has been taken into account. In CH_2OH^+ the electron populations in the d-orbitals of carbon and oxygen are 0.11 and 0.09 electrons, respectively. For CH_2SH^+ d-orbitals contribute 0.07 electrons to carbon and 0.13 electrons to sulphur.

‡ π-Electron transfers were calculated from the gross orbital populations of the $2p(C^+)$ orbital in CH_2XH^+. σ-Electron transfers were calculated using the equation: $\sigma_t = 1 - \pi_t - q_{CH_2}$ where π_t is the π-transfer to the CH_2 group and q_{CH_2} is the charge on CH_2.

§ The energy of the $2p(C^+)$ orbital in CH_3^+ is -7.8 eV (3-21G).

¶ The relative weights of resonance structures (**6b**) (RW) were calculated (assuming that only CH_2=XH^+ and CH_2^+–XH contribute) according to the equation: (RW)(double-bond length in CH_2=X) + (1 − RW)(single-bond length in H_3C–XH) = C–X bond length in CH_2XH^+.

CH_2SH^+ [equations (3a) and (4a)], respectively. The different behaviour of OH and SH can be understood as follows. In the perpendicular conformers conjugation results form interactions with the 'sp^2-hybridized' lone pairs of S or O, and the above data suggest that the 'sp^2 lone pair' on oxygen is a better π-donor than that on sulphur. Similar behaviour has been noticed in other comparisons of second- and first-row elements, and was attributed to a larger s-contribution to the 'sp^2 hybride,' in molecules containing second-row elements.[28a,41] The higher resonance stabilization in the perpendicular conformation of CH_2OH^+ (**2a**) than in CH_2SH^+ (**2b**) suggests that *the barriers to rotation around the* C–X *bond cannot be used to estimate the degree of* π-*stabilization in the planar cations.* The rotation barrier in CH_2OH^+ underestimates the importance of such conjugation in comparison with that in CH_2SH^+.

Relationship between Cation Stability and Charge Dispersal.—The various critria already discussed point to the conclusion that, when bonded to a good π-acceptor such as CH_2^+, sulphur is a better donor than oxygen. In the thio-substituted cations the charge distribution is more balanced and the contribution of resonance structure (**6b**) is higher than in the corresponding alkoxy-substituted cations. If a correlation exists between carbenium ion stability and the electron density (or one of the related properties already mentioned), then CH_2SH^+ is expected to be more stable than CH_2OH^+. However, both experiment and theory show that the stabilities of the two cations are comparable. *These results demonstrate that the correlation between the* π-*donation ability or the degree of charge dispersal and the stability of a carbenium ion is very limited, and should be used with extreme caution.* In particular, it appears that *this correlation does not hold when comparing first- and second-row elements.* Similar comments have been made previously. For example Delbecq[42] showed that even large π-delocalization, as in $HC{\equiv}CCH_2^-$ and $NCCH_2^-$, is not always accompanied by strong π-stabilization. Similarly, Apeloig *et al.*[43] pointed to the different stabilities of $CH_2{=}COH^+$ and $CH_2{=}CSH^+$, although the degree of π-conjugation in the two cations is very similar. Bernardi *et al.* have emphasized that 'σ-effects' (these 'σ-effects' are different from the σ-charge transfers already discussed) that favour OH over SH play a significant role in determining their stabilization energies.[16a]

Conclusions

(*a*) Relative to the corresponding hydrocarbons, CH_2OH^+ and CH_2SH^+ have comparable stabilities. Thus, OH and SH stabilize carbenium ions to a comparable degree, hydroxy being more stabilizing by *ca.* 2 kcal mol^{-1}.

(*b*) When the chlorides ($HXCH_2Cl$; X = O or S) are used as precursors to the cations, the cation $HSCH_2^+$ is predicted to be more stable than $HOCH_2^+$ by *ca.* 2.9 kcal mol^{-1}, as a result of substantial ground-state stabilization of $ClCH_2OH$ relatively to $ClCH_2SH$. This result is in agreement with recent ICR experiments.[6a]

(*c*) The deduction of the relative stabilities of carbenium ions from the degree of π-donation by the substituents or from other similar charge-related criteria should be treated with extreme caution, in particular when first- and second-row substituents are compared.

(*d*) The energies of the isodesmic reactions involving the carbocations $RXCH_2^+$ show strong basis set dependency; small split-valence basis sets overestimate considerably the stability of CH_2OH^+ relative to CH_2SH^+ (see also Appendix).

Appendix

It is of interest to examine in more detail the operation of the different basis sets and the effect of correlation energy on the calculated relative stabilities of $HSCH_2^+$ and $HOCH_2^+$.

Equations (5a and b), although isodesmic,[23b] show an unusually large basis-set dependence (Table 2). In particular the split-valence basis sets (*e.g.* 3-21G) considerably underestimate the stabilities of the thio-substituted cations.† We find that the underestimation of the cationic stabilization effect by second-row substituents *vs.* the isoelectronic first-row substituents is not specific to O and S, but is a more general phenomenon; *e.g.* in comparing $H_3SiCH_2^+$ with $CH_3CH_2^+$.[33c] A similar phenomenon is observed for the silenium ions $HSSiH_2^+$ and $HOSiH_2^+$.[44] This unusually large effect is not due to the neutral molecules in equations (5) as the energies of equations (6) and (7) do not change much with the basis set (Table 2). The strong basis-set dependency of equations (5a and b) probably results from the incorrect description by 3-21G of species which include conjugation between an empty p-orbital and an adjacent lone pair (*e.g.* $HSCH_2^+$). As similar situations may occur in other related problems, we have examined whether the poor operation of the 3-21G basis set results from its small size or from the absence of polarization functions (PF) and electron correlation energy (CE).

The Size of the Basis Set.—We have calculated equations (3a), (4a), and (5a) with the 6-31G basis set. We find that CH_2OH^+ is destabilized at 6-31G relative to 3-21G [ΔE(3a) = −45.8 and −52.6 kcal mol^{-1}, respectively], while the same change in the basis sets has almost no effect on the stability of CH_2SH^+ [ΔE(4a) = −32.6 and −31.8 kcal mol^{-1} at 6-31G and 3-21G, respectively]. Thus, the net result of increasing the size of the split-valence basis from 3-21G to 6-31G is to lower the stability of CH_2OH^+ by 7.6 kcal mol^{-1} relative to CH_2SH^+, closing *ca.* half of the gap in ΔE(5a) between 3-21G and 6-31G*. The remaining difference results from the absence of PF and CE.

Polarization Functions (PF).—To examine the effect of PF we have calculated the energies of equations (3a), (4a), and (5a) using a 3-21G basis set augmented with the standard set of six d-type functions[20a] in three different ways: (*a*) 3-21G$^{(*)}$ where only second-row atoms are augmented with PF; (*b*) 3-21G$^{(*)}$(O) where both sulphur and oxygen are augmented with PF; (*c*) 3-21G* (see Method section) where all first- and second-row elements are augmented with PF. The calculated energies using these augmented 3-21G basis sets are given in Table 2. Let us evaluate the importance of the addition of d-functions on carbon, oxygen, and sulphur[45] by expressing ΔE of equations (3a) and (4a) as the sum of ΔE_1 and ΔE_2, where $\Delta E_1 = E(CH_4) - E(CH_3^+)$ and $\Delta E_2 = E(CH_2XH^+) - E(CH_3XH)$ (X = O or S). We find that the addition of PF has a small effect on ΔE_1, *i.e.* $\Delta\Delta E_1 = [\Delta E_1(\text{3-21G}) - \Delta E_1(\text{3-21G*})] = 2.3$ kcal mol^{-1}, leading to the conclusion that the addition of d-functions on carbon is relatively unimportant. However, a much larger effect on ΔE_2 is observed, *i.e.* $\Delta\Delta E_2 = [\Delta E_2(\text{3-21G}) - \Delta E_2(\text{3-21G*})] = 8$ and 16.2 kcal mol^{-1} for X = OH or SH, respectively. The somewhat unexpected conclusion is that the addition of PF on oxygen is of significant importance; it contributes *ca.* half the effect observed when adding PF on sulphur. Thus, relative to 3-21G at 3-21G$^{(*)}$(O) and 3-21G*, CH_2OH^+ is more stabilized by 8.0 and 8.9 kcal mol^{-1}, respectively [equation (3a), Table 2] and CH_2SH^+ is more stabilized by 14.9 kcal mol^{-1} [equation (4a), 3-21G*]. The energy of equation (5a) which compares the stability of CH_2SH^+ with that of CH_2OH^+ is lowered (relative to 3-21G) when any of the above basis sets is used, *i.e.*

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† It is curious that the STO-3G energies are much closer to reality than the 3-21G energies [*e.g.*, ΔE(5a) = −1.5 kcal mol^{-1} at STO-3G//STO-3G, 20.8 kcal mol^{-1} at 3-21G//3-21G and 2.4 kcal mol^{-1} at MP3/6-31G*//3-21G].

ΔE(5a) = 20.8, 14.8, 14.0, or 6.0 kcal mol^{-1} at 3-21G, 3-21G*, 3-21G$^{(*)}$(O), and 3-21G$^{(*)}$, respectively. Note that at 3-21G$^{(*)}$, which is the least complete basis set, the energy of equation (5a) is the lowest, very close to the energy calculated with the larger and more complete 6-31G* basis set. However, this energy lowering is artificial because the 3-21G$^{(*)}$ basis set ignores the important stabilizing effect of PF on CH_2OH^+ but takes into consideration this effect for CH_2SH^+. The addition of PF on all heavy atoms decreases ΔE(5a) from 20.8 at 3-21G to 14.8 at 3-21G*//3-21G*, thus stabilizing CH_2SH^+ relative to CH_2OH^+ and closing *ca.* half of the gap in ΔE(5a) between 3-21G and 6-31G* The same effect of PF is observed when comparing 6-31G with 6-31G* [Table 2, equations (3a), (4a), and (5a)]; ΔE(5a) decreases from 13.2 kcal mol^{-1} at 6-31G to 8.4 kcal mol^{-1} at 6-31G*. Inspection of ΔE (5a) at 3-21G, 6-31G, and 3-21G* reveals additivity in the effects of the basis set expansion and of the addition of PF, so that ΔE at 6-31G* can be estimated according to equation (10).

$$\Delta E(\text{6-31G*}) = \Delta E(\text{3-21G}) - \{[\Delta E(\text{3-21G}) - \Delta E(\text{3-21G*})] + [\Delta E(\text{3-21G}) - \Delta E(\text{6-31G})]\} \quad (10)$$

Electron Correlation Energy.—The addition of correlation energy (at the MP2 or MP3/6-31G*//3-21G level) stabilizes both cations, but the effect is larger in CH_2SH^+ than in CH_2OH^+ [Table 2, equations (3) and (4)], reducing ΔE(5a) from 8.4 kcal mol^{-1} at 6-31G*//3-21G to 2.4 kcal mol^{-1} at MP3/6-31G*//3-21G.

Bernardi *et al.* reached similar conclusions regarding the effect of electron correlation energy and PF, but they have compared only 6-31G with 6-31G*, and have not evaluated the effect of increasing the size of the split-valence basis set.[16a]

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