Silyl Enol Ether 19. A solution of lithium tetramethylpiperidide (LTMP) was prepared by addition of 1.5 M *n*-BuLi in hexane (145 μL, 0.22 mmol) to a solution of tetramethylpiperidine (TMP) (37 μL, 0.22 mmol) in 0.5 mL of THF at 0 °C. After the reaction mixture was stirred for 15 min, the solution was cooled to –78 °C and TMS-Cl (31 μL, 0.24 mmol) was injected by syringe. The pyrrolidine **2a** (24 mg, 0.08 mmol), dissolved in 0.5 mL of THF, was added dropwise, over a period of 1 min. The solution was stirred for 15 min before quenching at –78 °C with Et_3N followed by $NaHCO_3$ (aqueous). The solution was poured into $NaHCO_3$ (aqueous) and extracted with CH_2Cl_2. The solution was dried (K_2CO_3) and concentrated to give 30 mg (100%) of silyl enol ether **19**. The product, being hydrolyzed rapidly on silica gel, could not be purified further: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26–7.05 (m, 4 H), 4.01–3.94 (m, 1 H), 3.97 (m, 2 H), 3.18–3.09 (m, 1 H), 3.12 (dd, 1 H, J = 15.3, 4.0 Hz), 3.02 (dd, 1 H, J = 15.3, 10.0 Hz), 2.75 (d, 1 H, J = 8.0 Hz), 2.71 (s, 3 H), 2.7–2.63 (m, 1 H), 2.09–1.1 (m, 6 H), 0.16 (s, 9 H).

Silyl Enol Ether 20. A solution (0.2 M) of LTMP was prepared by adding *n*-BuLi (1.55 M in hexane, 750 μL, 1.16 mmol) to TMP (205 μL, 1.22 mmol) in 5 mL of THF at 0 °C and stirring the mixture at this temperature for 30 min. A separate solution of **2a** (32 mg, 0.11 mmol) and TBDMS-Cl (130 mg, 0.86 mmol) in 2.2 mL of THF/HMPA (10:1) was prepared and cooled to –25 °C. A 500-μL portion of the LTMP solution was added dropwise to the stirred mixture of **2a** and silyl chloride. A 250-μL portion was added after 15 min, and after 15 min more, a further 200 μL was added. After the mixture was stirred for an additional 10 min, TLC indicated the reaction to be complete. The reaction mixture was diluted with NEt_3 (2 mL) and partitioned between $NaHCO_3$ (aqueous) and Et_2O. The organic layer was washed with water and brine and then evaporated. The product was purified by preparative TLC on silica gel (25% EtOAc/hexane) to obtain **20** (32 mg, 72%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25–7.05 (m, 4 H), 3.98 (m, 1 H), 3.95 (m, 2 H), 3.17–3.00 (m, 3 H), 2.78–2.62 (m, 2 H), 2.70 (s, 3 H), 2.03–1.58 (m, 6 H), 0.91 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 159.3, 142.1, 134.1, 128.1, 127.3, 126.1, 126.0, 89.8, 75.4, 62.5, 54.8, 51.0, 44.3, 41.3, 39.5, 38.3, 31.8, 25.7, 18.0, –4.7 (2 C); IR 2955, 2856, 1290, 1253.

Synthesis of Morphinan 1 from 20. A. Using $AgBF_4$. To a solution of **20** (54 mg, 0.13 mmol) in 3 mL of toluene was added $AgBF_4$ (56 mg, 0.29 mmol) in 2 mL of toluene. A precipitate of AgCl began to form immediately. The mixture was stirred in the dark for 20 min and then diluted with CH_2Cl_2 and $NaHCO_3$ (aqueous). The mixture was then filtered through Celite and the aqueous phase extracted with additional CH_2Cl_2. The organic phase was dried (K_2CO_3), evaporated, and the product purified by preparative TLC on silica gel (eluting with 12% MeOH/CH_2Cl_2) to obtain **1** (19 mg, 56%) identical in all respects with that prepared from enone **16**.

B. Using $AgSbF_6$. A solution of **20** (24 mg, 0.06 mmol) in toluene (2 mL) was treated with $AgSbF_6$ (50 mg, 0.14 mmol) and stirred for 30 min at 25 °C. Product isolation was accomplished in the same manner as described for the $AgBF_4$-mediated reaction (part A). The yield of **1** was 9.7 mg (64%).

Acknowledgment. We are grateful to the Research Board of the University of Illinois, Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this work.

Registry No. (±)-1, 113777-44-9; (±)-**2a**, 113777-45-0; (±)-**2a** (ketal), 113777-69-8; (±)-**2b**, 113830-02-7; (±)-**2b** (ketal), 113830-03-8; (±)-**3**, 113777-46-1; **5**, 37865-96-6; (±)-**6**, 113777-48-3; (±)-**6** (acid), 113777-63-2; (±)-**7**, 113777-49-4; (±)-**8**, 113777-50-7; **8** (nitro-aldol), 113777-64-3; (±)-**9**, 113777-51-8; (±)-**9** (*N*-trifluoroacetyl deriv), 113777-65-4; (±)-**10**, 113777-52-9; (±)-**10** (X = $COCf_3$), 113777-66-5; (±)-**11**, 113777-53-0; (±)-**11** (ketal), 113777-70-1; (±)-**12**, 113777-54-1; (±)-**12′**, 113777-68-7; (±)-**13**, 113777-55-2; (±)-**14**, 113777-56-3; (±)-**15**, 113777-57-4; (±)-**16**, 113777-58-5; (±)-7β-**17**, 113777-59-6; (±)-7α-**17**, 113777-47-2; (±)-7β-**17** (thiocarbonylimidazolide), 113777-67-6; (±)-**18**, 63783-50-6; (±)-**19**, 113777-60-9; (±)-**20**, 113777-61-0; (±)-1,4-dihydro-1-naphthoic acid, 113777-62-1.

An ab Initio Molecular Orbital Study of Acetyl Ions XCH_2CO^+, H_3CCS^+, H_3SiCO^+, and H_3CSiO^+

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Structures and energies of acetyl cations XCH_2CO^+, where X is H, CH_3, NH_2, OH, and F, have been obtained by using ab initio molecular orbital calculations with a 6-31G* basis set. With the exception of $H_2NCH_2CO^+$, which dissociates into CO and $H_2CNH_2^+$, all XCH_2CO^+ ions are the global minima on their respective surfaces. The MP2/6-31G**//6-31G* energy for elimination of CO from H_3CCO^+ is 81.8 kcal/mol (experimental 84.6 kcal/mol) but substitution of one hydrogen greatly decreases the dissociation energy. At the Hartree–Fock 6-31G* level the dissociation energy of $HOCH_2CO^+$ is close to zero but inclusion of correlation energy (MP2/6-31G*) has the effect of shortening the C–C bond and increasing the dissociation energy to 12.8 kcal/mol. The thioacetyl ion is the global minimum on the $C_2H_3S^+$ surface and cleavage of the C–C bond to form CH_3^+ and CS has a higher energy (125.6 kcal/mol). On the $SiCH_3O^+$ surface structures have been optimized for six isomers and for three pairs of dissociation products. The β-sila acetyl ion, H_3SiCO^+, is higher in energy than the global minimum $H_3CO^+{=}Si$ by 25.8 kcal/mol. For 1,2-shifts of SiH_3 in H_3SiCO^+ and CH_3 in H_3CSiO^+ the transition structures have very long bonds and are close in energy to the dissociation products.

Acylium ions RCO^+ have long been thought to be the intermediates in Friedel–Crafts acylation reactions[1] and in the decarbonylation of carboxylic acids in concentrated mineral acids. More recently many acylium ions have been observed under stable ion conditions in superacid solutions.[2] Acylium ions are also common species in the gas phase. They are produced in the mass spectrometric decomposition of most ions containing carbonyl groups and the simplest acylium ion, HCO^+, along with the isomeric

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[1] *Friedel–Craft and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1963; Vol. 1.

[2] Olah, G. A.; Germain, A.; White, A. M. *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R. Eds.; Wiley Interscience: New York, 1976; Vol V, p 2049.

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Table I. Structural Parameters from 6-31G Optimization and Total Energies (hartrees) for Acylium Ions XCH_2CO^+

		bond length (Å)				
X	point group	C–C	C–O	C–X	6-31G*	MP2/6-31G**
H	C_{3v}	1.465 (1.452)[a]	1.095 (1.109)[a]	1.085	−152.05929	−152.49489
CH_3	C_s	1.473	1.096	1.548	−191.10297	−191.98408
NH_2	C_s	1.565	1.095	1.401	−207.08341	−207.68843
OH	C_1	1.574	1.094	1.347	−226.89318	−227.50493
F	C_s	1.546	1.092	1.320	−250.86985	−251.46218

[a] Experimental bond lengths, ref 34.

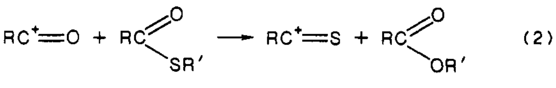
HOC^+, has been observed in interstellar clouds.[3,4]

In solution tertiary acylium ions undergo decarbonylation to form alkyl cations (eq 1). Also primary acylium

$$RC^+{=}O \rightarrow R^+ + CO \qquad (1)$$

ions which contain electron-donating substituents, e.g., methoxy[5-7] and phenoxy,[8,9] readily eliminate carbon monoxide to form the methyl cations $R'OCH_2^+$.

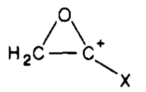
Alkanethioic acids and esters in superacid solutions[10] do not form thioacylium ions RCS^+, but arylthioacylium cations are generated by the reaction of thiobenzoyl chlorides with silver.[10,11] These observations indicate that thioacylium ions are less stable than acylium ions but in the gas phase ICR work has shown that acylium ions CH_3CO^+ and $H_3CCH_2CO^+$ react with thioic acids and esters to produce thioacylium ions[12] (eq 2). The mass



$$RC^+{=}O + RC(=O)SR' \rightarrow RC^+{=}S + RC(=O)OR' \qquad (2)$$

spectra of a wide variety of organosulfur compounds contain a common ion, $C_2H_3S^+$, and ab initio molecular orbital calculations show the thioacetyl cation H_3CCS^+ to be the global minimum on this energy hypersurface.[13,14] The simplest of the thioacylium ions, HCS^+, has been observed in interstellar clouds[15,16] and in mass spectroscopy.[17]

In a recent theoretical study of carbocations containing α-carbonyl substituents, we have found the oxiranyl, **1**, and acylium, **2**, ions to be at minima on the energy hypersurface



1

XH_2CCO^+

2

(X = H, CH_3, OH, F).[18] On each surface the acylium ion is the global minimum, except when X is NH_2, where the dissociation products, $CH_2NH_2^+$ and CO, are lower in energy. Here we present our results on monosubstituted acetyl cations, the thioacetyl cation, and ions H_3SiCO^+.

Table II. Energy (kcal/mol) for Reaction $XCH_2CO^+ + CH_4 \rightarrow CH_3X + CH_3CO^+$

X	6-31G*	MP2/6-31G**	X	6-31G*	MP2/6-31G**
CH_3	6.3	6.6	OH	−4.0	−4.2
NH_2	5.9	5.2	F	−18.1	−17.4

Method and Results

Standard ab initio calculations have been carried out by using the MONSTERGAUSS[19] and GAUSSIAN 82[20] programs. Structure optimization using gradient techniques was performed at the Hartree–Fock (HF) level of theory using the 6-31G* basis set.[21] Improved energies were obtained by using single point calculations at the 6-31G** level[21] and including valence electron correlation calculated by second-order Møller–Plesset perturbation theory.[22,23] These latter calculations are denoted as MP2/6-31G**//6-31G*. Transition structures were crudely located by using a point-by-point method and then refined by using the VAO5AD method.[24]

1. Ions XH_2CCO^+. The parent acylium ion, H_3CCO^+, has C_{3v} symmetry and the C–O bond (1.095 Å, Table I) is slightly shorter than that of carbon monoxide (1.110 Å at 6-31G*). The methyl group carries a charge of +0.44 and the C–C bond (1.465 Å) is shorter than the average single C–C bond (1.54 Å[25]), indicating that there is considerable hyperconjugative donation from methyl to π^* of the carbonyl.

When one of the hydrogen atoms of the methyl group is replaced by π donors NH_2, OH, and F, the length of the C–C bond increases dramatically (by ~0.1 Å). In these β-substituted acetyl cations the conformations adopted by amino and hydroxy maximize the π-donation from the lone pair on X to CH_2CO^+. The LUMO of the acetyl cation is bonding between the cations and antibonding between C and O and interaction with π donors X (structure **3**) then should result in a shortening of C–X and an increase in charge on CH_2X (both observed). However, both CO^+ and X are strongly σ-withdrawing (structure **4**) and the overall effect is destabilizing and results in a weakening of the C–C

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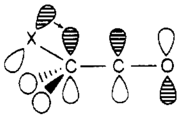
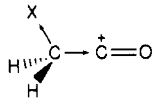
Table III. Energy (kcal/mol) for Elimination of CO from XCH_2CO^+

X	6-31G*	MP2/6-31G**	expt[a]
H	57	81.8	84.6
CH_3	34.9	47.1	48.6
NH_2	−23.6	−12.8	
OH	−0.7	11.5	
F	24.0	38.7	

[a] Reference 28.

bond. In the isoelectronic FCH_2CN the geminal interaction between F and CN is destabilizing by 4 kcal/mol.[26]


π donor, π acceptor
3


two σ acceptors
4

The unusual effect of substitution on the structure of the acylium ion may also be explained in terms of contributions from resonance structures. For acylium ions XH_2CCO^+, π donation leads to stabilization of the dissociation products CO and XCH_2^+ and, at the HF level of theory when X is NH_2 and OH, dissociation is exothermic. However, local minima exist for all the acylium ions and the long C–C bonds found for ions containing π donors indicate that no-bond resonance structures are important contributors.

$$\ddot{X}CH_2\overset{+}{C}{=}O \leftrightarrow \overset{+}{X}{=}CH_2\ {:}C{=}O$$

The effect of substituents in the acetyl cation (Table II) can be assessed by using the isodesmic reaction in eq 3.

$$XCH_2CO^+ + CH_4 \rightarrow H_3CX + H_3CCO^+ \qquad (3)$$

The methyl group, which functions as a weak σ and π donor, is weakly stabilizing. The amino group, a strong π donor, is also weakly stabilizing but this contrasts with the large stabilization energy by amino in the methyl cation (~100 kcal/mol[27]). Hydroxy and fluoro are stronger σ acceptors and weaker π donors and are destabilizing in the acetyl cation.

The weakness of the C–C bond resulting from geminal interaction in XCH_2CO^+ and the stabilizing effect of these same substituents in methyl cations CH_2X^+ result in a pronounced substituent effect for the elimination of CO from acetyl cations (Table III). At the HF level the barriers to elimination of CO from $H_2NCH_2CO^+$ and $HOCH_2CO^+$ are very low (~0.1 kcal/mol) and the products are lower in energy than the acetyl ions. Inclusion of correlation energy is necessary for an adequate description of this bond-breaking reaction and there is good agreement between the experimental data[28] and the MP2 results for H_3CCO^+ and $H_3CH_2CCO^+$. At the MP2 level the hydroxy-substituted ion is lower in energy (by 11.5 kcal/mol) than its dissociation products but the lack of a barrier to dissociation may make it hard to detect by experiment. In this context it is interesting to note that methoxy-[6,7] and phenoxyacetic[8,9] acid derivatives are decarbonylated in concentrated mineral acids.

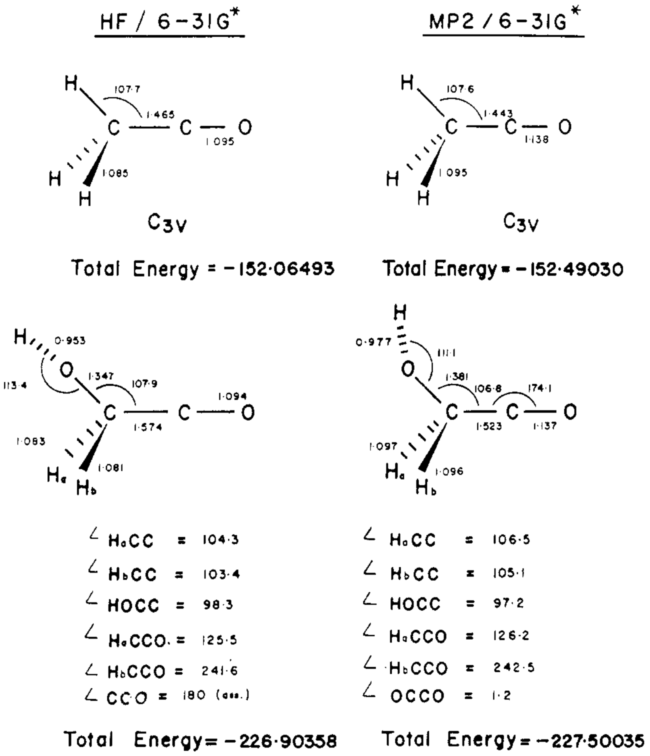


Figure 1. Structures of acylium ions optimized at 6-31G* and MP2/6-31G* levels. Bond lengths in Ångstroms and angles in degrees.

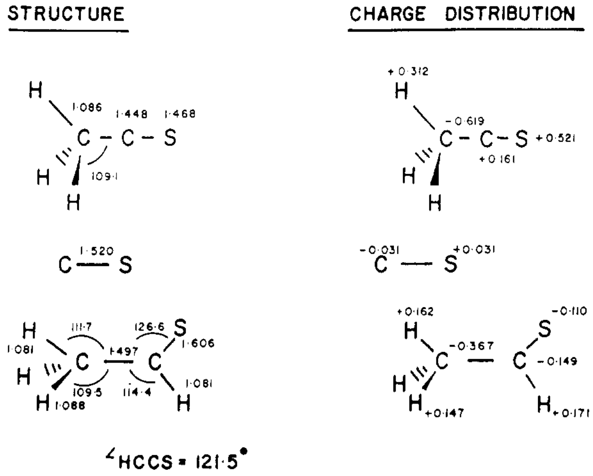


Figure 2. Optimized structures and charge distributions for thioacetyl ion, thioacetaldehyde, and carbon monosulfide from 6-31G* level calculations.

2. Structural Optimization at MP2/6-31G*. Molecules containing atoms to the right of the Periodic Table have many valence electrons. Consequently many excited states of these molecules are antibonding and inclusion of correlation energy results in increases in bond lengths.[26] For the acetyl cation the LUMO is antibonding in C–O and C–H but bonding in C–C. The structural changes introduced by using MP2/6-31G* level calculations for optimization, an increase in C–O and C–H and a decrease in C–C, reflect this character (Figure 1).

Inclusion of correlation energy has a more pronounced effect on the structure of the β-hydroxyacetyl cation. Here C–C is shortened by 0.051 Å, and C=O and C—OH are lengthened by 0.043 Å and 0.034 Å, respectively. At the MP2/6-31G* level with all electrons included and all structural optimization carried out at this level, the energy for the elimination of CO is 12.8 kcal/mol.

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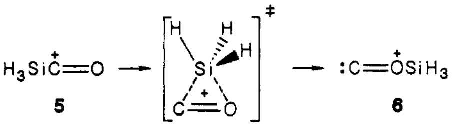
3. The Thioacetyl Ion. The thiocarbonyl group has poor 2p–3p π overlap and consequently has less double-bond character than the carbonyl group.[29] The C–S bond in the thioacetyl cation is 0.14 Å shorter than that in thioacetaldehyde (Figure 2), the sulfur atom carries a large positive charge (+0.521) and the ion is best represented by the structure $H_3CC{\equiv}S^+$. The C–C bond in this ion is shorter and stronger than that in CH_3CO^+ (ΔE for heterolytic cleavage to form CH_3^+ are 125.6 and 81.8 kcal/mol, respectively, at the MP2 level). There is less positive charge on the methyl group of the thioacetyl ion and if these ions are viewed as complexes between the diatomics CS and CO with CH_3^+, then CS is the more effective ligand.

In the gas phase acylium ions react with thioic acids and esters to give thioacylium ions.[12] At the Hartree–Fock level reaction 4 is almost thermoneutral (ΔE is 3.4 kcal/mol) and when correlation energy is included ΔE is −4.7 kcal/mol.

$$H_3CCO^+ + H_3CCHS \rightarrow H_3CCS^+ + H_3CCHO \qquad (4)$$

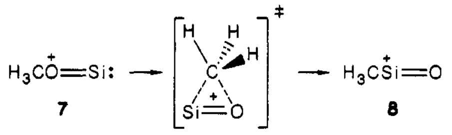
4. H_3SiCO^+ and Isomers. Silicon is more effective at carrying a positive charge than carbon and in H_3SiCO^+, **5**, the majority of the positive charge (+0.755) is on the SiH_3 group. The Si–C bond (2.069 Å) is longer than that



of methylsilane (1.867 Å[30]) and heterolytic cleavage into SiH_3^+ and CO requires less energy (39.5 kcal/mol) than elimination of CO from CH_3CO^+ (81.8 kcal/mol). Conversely the silyl cation affinity of CO is lower than the methyl cation affinity and previous theoretical work[31] has shown that bases NH_3, PH_3, H_2O, and H_2S all have lower affinities for the silyl cation.

The silicon–oxygen bond is strong and ion **6**, where the silyl cation has added to the oxygen of CO, is only 18.8 kcal/mol higher in energy than H_3SiCO^+. This compares with an energy difference of ~50 kcal/mol between H_3CCO^+ and $COCH_3^+$.[32]

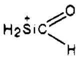
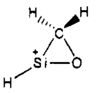
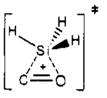
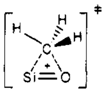
Oxygen-methylated silicon monoxide **7** is the global minimum, 25.8 kcal/mol below **5**. The silicon-methylated



isomer **8** is 30.3 kcal/mol higher in energy and SiO then behaves differently from CO and CS in that alkylation preferentially occurs at the group VI element. Protonation of SiO also occurs at oxygen (the difference in basicities is 66.5 kcal/mol[33]).

The transition structures for interconversion of **5** and **6** and interconversion of **7** and **8** have extremely long bonds (Table IV). Furthermore both transition structures are close in energy to the separated electrophile (SiH_3^+ and CH_3^+) and diatomic (CO and SiO), indicating that interconversion of these pairs of isomers occurs essentially by separation and recombination. Similar behavior was found in the interconversion of CH_3CO^+ and $COCH_3^+$.[32]

Table IV. Relative Energies (kcal/mol) of Isomers on H_3CSiO^+ Surface

structure	symmetry	bond length (Å)	6-31G*/ 6-31G*	MP2/6-31G**// 6-31G*
$H_3CO^+{=}Si$[a,b]	C_{3v}	C–O 1.450 SiO 1.526	0	0
$H_3SiC^+{=}O$	C_{3v}	Si–C 2.069 C–O 1.096	19.9	25.8
$H_3SiO^+{=}C$	C_{3v}	Si–O 1.986 C–O 1.133	29.3	44.6
$H_3CSi^+{=}O$	C_{3v}	C–Si 1.851 Si–O 1.465	47.8	30.3
SiH_3^+ + CO	D_{3h}, $C_{\infty v}$		49.6	65.3
	C_s	Si–C 1.932 C–O 1.182	68.1	
	C_s	C–Si 1.792 C–O 1.506 Si–O 1.574	70.2	
CH_3^+ + SiO	D_{3h}, $C_{\infty v}$		85.6	78.3
HCO^+ + SiH_2 (singlet)	$C_{\infty v}$, C_{2v}		113.1	
	C_s	Si–C 3.073 Si–O 3.200 C–O 1.113	48.6	61.1
	C_s	C–Si 2.553 Si–O 1.481 C–O 2.983	85.2	73.8

[a] Total energy of $H_3CO^+{=}Si$ at 6-1G*//6-31G* is −403.14589 hartrees and at MP2/6-31G**//6-31G* −403.53585 hartrees. [b] The global minimum on the $CSiOH_2$ surface is cyclic. $\overline{SiCH_2O}$, and protonation of this molecule to form $H_3CO^+{=}Si$ has an energy of 239 kcal/mol at the MP2/6-31G**//6-31G* level.

Conclusions

Acylium ions XCH_2CO^+ are the global minima on most surfaces but when X is capable of stabilizing the methyl cation, then the energy for dissociation into XCH_2^+ and CO is lowered. An α-amino substituent is the most stabilizing group in carbocations and ion $H_2NCH_2CO^+$ dissociates without barrier into $NH_2CH_2^+$ and CO. At the post-Hartree–Fock level the energy required to eliminate CO from acylium ions is larger than that at the HF 6-31G* level and in the case of $HOCH_2CO^+$ the dissociation energy changes to 12.8 kcal/mol from approximately zero. These post-Hartree–Fock calculations are consistent with the experimental observation that methoxy- and phenoxyacetic acid derivatives undergo elimination of CO when heated in strongly acidic solutions.

Electrophiles H^+, CH_3^+, and SiH_3^+ all preferentially add to the carbon atom of CO, and H^+ and CH_3^+ add to the carbon of CS. Interconversion of the products of C and O addition proceeds via transition structures which have very long bonds between the migrating group and CO. Also the energies of the transition structures are close to those of CO and the electrophile, indicating that this 1,2-shift involves dissociation followed by recombination.

Electrophilic addition to SiO occurs preferentially on oxygen and structure H_3COSi^+ appears to be the global minimum. Here also methyl migration to form OSi^+CH_3

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involves a transition structure with long bonds and with energy close to that of the products of CO elimination.

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Registry No. CH_3CO^+, 15762-07-9; $CH_3CH_2CO^+$, 17158-30-4; $NH_2CH_2CO^+$, 113925-08-9; $HOCH_2CO^+$, 51583-45-0; FCH_2CO^+, 51583-46-1; $H_3CO^+{=}Si$, 113925-09-0; $H_3SiC^+{=}O$, 113925-10-3; $H_3SiO^+{=}C$, 113925-11-4; $H_3CSi^+{=}O$, 113925-12-5; CH_4, 74-82-8.

Oxidation of Substituted Benzyl Alcohols by Pyridinium Fluorochromate: A Kinetic Study

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The kinetics of the oxidation of 30 monosubstituted benzyl alcohols to the corresponding benzaldehydes by pyridinium fluorochromate (PFC) have been studied. The reaction is first order with respect to PFC. A Michaelis–Menten type kinetics was observed with respect to the substrate, indicating the formation of a PFC–alcohol complex in the preequilibrium. The formation constants and the rates of disproportionation of the complexes were determined. The oxidation of [α,α-$^2H_2$]benzyl alcohol indicated the presence of a substantial primary kinetic isotope effect. The rates of the decomposition of the complexes of the meta- and para-substituted alcohols were analyzed in terms of Taft's and Swain's dual substituent parameter equations. The meta compounds showed an excellent correlation with Taft's σ_I and σ_R^0 values while the para-substituted compounds correlate with σ_I and σ_R^{BA} constants. The rates of the ortho-substituted alcohols correlate with Charton's equation of inductive, resonance, and steric parameters. The reaction was studied in 19 solvents. The correlation analysis of the solvent effect indicated the greater importance of the cation-solvating power of the solvent. The reaction involves a hydride ion transfer in the rate-determining step.

Pyridinium fluorochromate (PFC), a complex of chromic oxide, pyridine, and hydrogen fluoride,[1] is reported to be a more versatile oxidant than pyridinium chlorochromate (PCC).[2] Preliminary reports about the kinetics of the oxidation of alcohols[3] by PFC indicated that oxidations by PFC and PCC[4] follow different mechanistic pathways. In continuation of our earlier reports about the mechanism of the oxidation by PCC,[4] we report now the kinetics of the oxidation of some meta-, para-, and ortho-monosubstituted benzyl alcohols by PFC. Attempts have been made to study the correlation of organic reactivity in this reaction.

Table I. Rate Constants for the Oxidation of Benzyl Alcohol by PFC at 298 K in DMSO

10^3[PFC], M	[BA], M	10^5k_1, s^{-1}	10^3[PFC], M	[BA], M	10^5k_1, s^{-1}
0.5	0.02	5.10	2.0	0.08	17.3
1.0	0.02	5.00	2.0	0.10	20.7
2.0	0.02	5.07	2.0	0.15	27.8
3.0	0.02	5.03	2.0	0.20	33.6
4.0	0.02	5.13	2.0	0.40	48.8
5.0	0.02	5.02	0.20	0.60	57.5
2.0	0.04	9.06	0.20	1.00	67.7
2.0	0.06	13.6			

Experimental Section

(Acetylamino)benzyl alcohols were prepared by the reported methods.[5-7] The other alcohols (Fluka or Aldrich) were purified by either recrystallization or distillation. [α,α-$^2H_2$]Benzyl alcohol was prepared by the reduction[8] of ethyl benzoate by lithium aluminum deuteride (Fluka). PFC was prepared by the reported procedure.[1] The solvents were purified by the usual methods.[9]

Product Analysis. Benzyl alcohol (4.9 g, 0.05 mol) and PFC (2.0 g, 0.01 mol) were made up to 100 mL in DMSO. The reaction mixture was allowed to stand for ca. 12 h to ensure completion of the reaction. Most of the solvent was removed by distillation under reduced pressure. The residue was treated with an excess (250 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 M HCl and kept in a refrigerator for ca. 8 h. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The product was identical (mp and mixture mp) with an authentic sample of the DNP of benzaldehyde. The yields of DNP before and after recrystallization were 2.75 g (96%) and 2.57 g (90%) respectively. In similar experiments, with the other alcohols, the yields of DNP after recrystallization were 83–95%.

Kinetic Measurements. The pseudo-first-order conditions were attained by keeping a large excess of the alcohol over PFC. The temperature was kept constant to ±0.1 K. The reactions were followed both iodometrically and spectrophotometrically at 356 nm. Duplicate kinetic runs showed that the rate constants obtained by the two procedures agreed within ±2%. The reactions of the alcohols containing methoxy and acetylamino groups were very fast, and they were studied on a stopped-flow spectrophotometer (Hi-Tech, U.K.). The pseudo-first-order rate constant, k_1, was obtained from the linear plots of log [PFC] vs time. The kinetics were studied in dimethyl sulfoxide (DMSO), unless mentioned otherwise.

Results and Discussion

The rates and other data were obtained for all the alcohols investigated. Since results are similar, only repre-

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